

# ✓ GROUND STATE VIBRATIONAL ANALYSIS OF FEW AROMATIC HYDROCARBONS AND AMINO ACIDS: AN AB INITIO STUDY

*A Thesis Submitted*  
in Partial Fulfillment of the Requirements  
for the Degree of  
Doctor of Philosophy

*by*  
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*to the*  
DEPARTMENT OF CHEMISTRY  
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR  
December, 1996

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I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India under the supervision of Dr. S. Manogaran.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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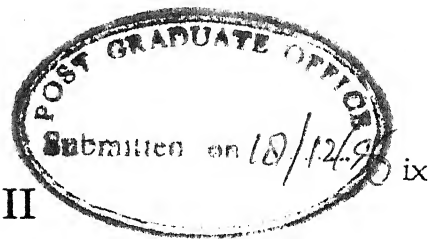
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# Acknowledgments

I wish to express my profound sense of gratitude to Dr. S. Manogaran for his excellent guidance and inspiration. The rare opportunity I got, to explore the vast frontiers of science was only possible under his astute guidance. His encouraging words and the kind of help he rendered on me during this five years of time is really appreciable.

I thank Professor N. Sathyamurthy for providing Gaussian programs and for his valuable suggestions and help during this period. I thank Professor P. K. Bharadwaj for his interest in my work and also for keeping a lively atmosphere in the lab. I really thank him for all the care and advice he gave me during my stay in the lab. I also want to express my thank to Dr. A. Chandra for his help at the time of need.

This work would not have been feasible had it not been for the cooperation and support I received from the computer center. I thank Professor H. Karnik, Dr. R. Tewari, Dr. K. S. Singh, Mr. A. Alam, Mr. N. Roberts, Mr. Y. D. S. Arya, Mr. H. P. S. Parihar and all the operating staff for the patience with which they bore my byte crunching computations.

Mrs. Geeta Manogaran, Divya and Kartik are fondly remembered for all their love and care they bestowed on me and make my stay a homely one.

I thank all my lab-mates Indrajit, Pradyut, Dillip, Prasun, Gopal, Janmejaya, Vaibhav and Bappaditya and also all my friends of Chemistry Department. I should really thank Nilu, Biswajit, Sanjib and Shirshendu for helping me at the final stage of processing the thesis. Special thanks to all my C-top friends Tapo, Tapan, Debada, Manoj and Prasen for making life more kaleidoscopic during my stay at Hall V. Subit, Sankarda, Arun, Swapanda, Abirda, Kishore, Mama and all members of our drama troop and also to host of other friends who are already left should be thanked for making life a memorable one at various stages here.

I am grateful to my elder brother for his constant inspiration and mental support at every step of my work.

Last but not the least is the constant encouragement and love I received from Sangita, as a friend and my wife, which always kept me cheerful and enthusiastic even at the crucial stage of this work.

Debashis Chakraborty

# Synopsis

An accurate knowledge of molecular force fields is essential in the prediction and interpretation of vibrational spectra and also in molecular mechanics and dynamics simulation [1]. Attempts to deduce molecular force field from spectral data alone have not been successful so far for molecules containing more than a few atoms [2]. Ab initio molecular orbital methods offer an attractive alternative to resolve this problem. Due to the recent advances in the quantum chemical methodology, an accurate description of molecular force field is possible for small molecules by extending the atomic orbital basis sets and including the electron correlation. Such a physical representation of systems of interest in chemistry and structural biology is not possible due to limited computational resources. A new approach has been introduced in this regard by using the ab initio Hartree-Fock calculations employing an optimal basis set to derive preliminary quantum mechanical force field, whose parameters are then systematically scaled by fitting the available experimental data. These scale factors are then transferred to structurally related larger systems [3]. In the present study, a new algorithm has been developed in this regard and interpretation and prediction of the vibrational spectra of few aromatic hydrocarbons [4] and amino acids have been carried out using this newly developed methodology.

In chapter 1 of the thesis, the use of ab initio calculations in the development of force field has been reviewed. Importance of the force constants for the interpretation and prediction of vibrational spectra has been discussed and the existing methodologies on scaling of ab initio force field have been reviewed along with their advantages and disadvantages. A brief outline of the thesis is also presented.

In chapter 2, the basic framework of ab initio calculations has been presented. A brief description of the basis sets employed, the Hartree-Fock model, methods of inclusion of

electron correlation and the theory behind the evaluation of force constants is given. The conversion of cartesian force constants (available from ab initio studies) to non-redundant local and symmetric force constants is also discussed. All the ab initio calculations have been carried out with Gaussian and GAMESS suit of programs.

In chapter 3, a novel method is described to obtain a scale factor for each force constant in the force constant matrix as a quantitative measure of the systematic error in the ab initio methods. These scale factors offer a simple solution to the problem of interpretation and prediction of vibrational spectra using the Scaled Quantum Mechanical (SQM) approach of Pulay et al. [3]. A detailed description of the methodology and its theoretical justification are presented. The advantages of the present methodology over the existing ones are listed. The performance of the method compared to the SQM procedure is demonstrated by using acrolein as example. A nearly unique force field of benzene is obtained by fitting the ab initio force field of five different calculations (HF/4-21G, 6-31G\*, 6-311G\*\*, 6-311++G\*\* and MP2/6-311G\*\*) to the harmonic frequencies of Ozkabak and Goodman [5]. Transferability of the scale factors for the prediction of vibrational spectra has been demonstrated by using pyridine and benzaldehyde as test cases.

In chapter 4, a complete set of force constants and their corresponding scale factors are obtained by fitting the experimental frequencies of naphthalene-d<sub>0</sub> and -d<sub>8</sub> to the ab initio force field obtained at HF/4-21G level using the methodology described in chapter 3. The fitting is extremely successful in producing a force field which reproduces the frequencies within an average deviation of 5.7 cm<sup>-1</sup> for naphthalene-d<sub>0</sub> and 4.0 cm<sup>-1</sup> for -d<sub>8</sub> from the experimentally observed fundamentals. The ab initio force constants of anthracene are obtained using the same level of theory and scaled using the scale factors of naphthalene. The earlier assignments are either confirmed or reassigned utilizing the frequencies and potential energy distributions (PED) derived from the scaled force field. The agreement between the experimental and predicted fundamentals are excellent for this molecule containing 24 atoms giving an average deviation of 8.2 cm<sup>-1</sup>.

In chapter 5, the force fields of glycine hydrochloride (GH) and glycyglycine hydrochloride (GGH) are presented. A conformational study was undertaken for GGH at HF/6-31G\*\* level of theory. By fitting the experimental vibrational frequencies of seven

isotopomers of GH to the ab initio force field for the lowest energy conformation using the methodology described in chapter 3 a complete set of force constants and their corresponding scale factors are obtained. The fitting is extremely successful in producing a force field with an average deviation of  $9.7\text{ cm}^{-1}$  from the experimentally observed fundamentals for all the seven isotopomers. The scale factors of GH are used to obtain the scaled ab initio force field of the minimum energy conformer of GGH, which in turn was used to predict the vibrational frequencies and their PED. The very good agreement between the experimental and predicted fundamentals offer a "real" example to the concept of building a reliable force field from a smaller unit to a larger unit i.e. of a dipeptide from its parent amino acids.

In chapter 6, transferability of scale factors from smaller constituents to a larger is successfully attempted for two important amino acid hydrochlorides cysteine and serine. The scale factors of GH from chapter 5 are used to scale the ab initio force field of both the molecules. Scale factors of the side chain residues of cysteine and serine are obtained by fitting the ab initio force field of ethanethiol and ethanol to their respective experimental frequencies at the same level of theory. In both the cases the prediction of the frequencies and their normal mode descriptions are very good. This further indicates that the scale factors of structurally related small organic molecules (ethanethiol and ethanol in the present case) can be used to mimic the right features of the amino acid side chain residues.

In chapter 7, the ab initio calculation of isolated glycine zwitterion to study the vibrational spectral features is presented. Such an ab initio calculation on amino acids do not reproduce the experimental PED of the normal modes because of the strong intramolecular H-bonding which is absent in the condensed phase. Using Onsager reaction field model with a proper choice of solute radius and dielectric constant, it is shown that the ab initio method mimics the features of experimental PED very well. Several basis sets are used for identifying the right ab initio model. By fitting this ab initio force field of the solvated model to the experimental vibrational frequencies of four different isotopomers at HF/6-31++G\* level a complete set of non-redundant force constants are obtained. The fitting produced a force field which produces the frequencies with an average deviation of  $7.9\text{ cm}^{-1}$  from the experimentally observed fundamentals of all the four isotopomers.

Since most of the experimental data on amino acids are available for solution and/or solid phases, their correct interpretation requires a good theoretical model.

In chapter 8, based on our earlier glycine *ab initio* solvated model calculations, a complete set of scale factors are generated for alanine by fitting the *ab initio* solvated model force field to the experimental frequencies of five different isotopomers. These scale factors are then used to scale the *ab initio* force field of two important amino acids, cysteine and serine. Scale factors of the side chain residues of both cysteine and serine are obtained by fitting the *ab initio* solvated model force field of ethanethiol and ethanol to their respective experimental frequencies at the same level of theory. In both the cases the prediction of the frequencies and their normal mode descriptions are excellent compared to the size and complexity of the molecules.

In chapter 9, a summary of the findings of the present study and suggestions for future work have been forwarded.



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# Chapter 1

## Introduction

Numerical simulations of structures and dynamics of molecules serve as an invaluable complement to experiments due to the significant developments in new generation computers, improved programs and wide accessibility to these programs. Simulation of molecular force field as an important tool in the study of structure and dynamics of molecules rest on the hypothesis that the potential energy of a molecule or assembly of molecules can be reproduced by a low order Taylor series expansion in terms of internal coordinates. At the harmonic level the prediction of good vibrational spectra greatly enhances its use as a structural tool in cases where other structural methods such as NMR or diffraction methods cannot be applied, e.g. transient species, polymers, low temperature matrices, adsorbed layers or for structural phenomena which are fast in the NMR time scale. Improved thermodynamic functions can be obtained from the vibrational spectra whose fundamentals are correctly identified. Another important application of accurate force fields is the evaluation of the vibrational averaging effects on observed molecular properties, e.g. geometries, dipole moments etc. There is a great deal of interest in the field due to the recent technical developments of molecular spectroscopy [1-9].

Attempts to deduce molecular force fields from spectral data alone have not been successful so far for molecules containing more than a few atoms [10-12]. As the number of atoms increase, the number of force constants to be determined becomes more than the experimentally available frequencies and multiple solution becomes a problem. Ab initio calculations due to their firm theoretical basis tend to be more systematic and reliable, than other methods available for the development of force fields. With the advent of

faster computers and widely accessible programs, rapid strides have been made in the calculation of *ab initio* force fields at various levels of sophistication [13-20]. As an outcome, in the last decade, there has been a tremendous growth in the *ab initio* quantum mechanical calculation of force constants for polyatomic molecules and the prediction of vibrational spectra [21-30].

Due to the recent advances in the quantum chemical methodology, an accurate description of molecular force field is possible for small molecules by extending the atomic orbital basis sets and including electron correlation. Such a physical representation of a typically large macro molecular system of interest in structural biology is not possible due to the limited computational resources. As a result, the simulation of macromolecules such as proteins and nucleic acids and their interactions have led to a large number of empirical force fields through refinement of parameters and their transferability from small model systems [31-50]. Most of these currently available force fields involve the electrostatic potential and the solvation free energy as the focus of attention. These force fields are perfectly adequate to the applications of molecular recognition or identification of closely related minima. However, these force fields largely ignore the accurate reproduction of the vibrational frequencies [50]. The acceptability of the force field is apparently gauged by the agreement between the calculated and experimentally observed fundamental vibrational frequencies of the parent molecule and its isotopomers. Thus it seems that an accurate description of vibrational frequencies of some model compounds using theoretically sound methodology (*ab initio*) can provide improved force field parameters for a better description of molecular mechanics or molecular dynamics simulation of biologically important macromolecules.

Transferability of molecular force constants between structurally related molecules and refining them with the aid of experimental vibrational frequencies using normal coordinate analysis is known for long [51]. In this method the force constants are simply guessed based on their values in related molecules and modified so as to reproduce all the isotopic frequencies closely. *Ab initio* methods could give better force constants because they are evaluated based on firm theoretical basis [52,53]. However at the Hartree-Fock (HF) level of *ab initio* theory, finite basis set and neglect of electron correlation result in

over-estimated values of force constants and frequencies. Although highly sophisticated methods like CCSD(T) and CASS are capable of yielding more accurate harmonic force constants can not be applied on a routine basis to medium sized molecules. Even when accurate harmonic force constants become available, for prediction of experimental frequencies we need anharmonic force constants which involve the evaluation of cubic and quartic force constants.

As a reasonable solution to this problem use of both the experimental data and the ab initio information had been advocated. A new approach has been introduced in this regard by using the ab initio Hartree-Fock calculations employing an optimal basis set to derive a preliminary quantum mechanical force field, whose parameters are then systematically scaled by fitting them to the available experimental data [11,54-66]. All these approaches are based on the assumption that the errors involved in the ab initio calculations are fairly systematic. Analysis of the calculated harmonic force constants of a large number of molecules using HF theory leads to the following general conclusions [10].

- i) Diagonal stretching force constants are systematically overestimated by 10-15%.
- ii) Diagonal bending force constants are systematically overestimated by 20-30%, slightly higher than stretching.
- iii) For coupling constants the errors are less systematic, large values are reproduced within 10-30% and for small values an absolute error seems more appropriate, within 0.05-0.10 mdyne/Å.

The combination of theory and experiment in evaluating the force constants was first attempted by Pulay and Meyer through their simple scaling scheme of 10% reduction of the stretchings, 20% reduction for the bendings and the interaction terms left unchanged at their theoretical values [54]. Another procedure proposed by Botschwina et al. [55,56] and Pouchan et al. [58] involves fitting of the diagonal force constants to the experimental frequencies while the off-diagonal terms are taken from calculated results. Blom and Altona in their more detailed scaling scheme introduced separate scale factors for several types of distortions and also optimization of these scale factors by fitting them to the experimental frequencies in a least squares procedure [59]. Ha, Mayer and Günthard

proposed a relatively different scaling scheme of using both unscaled force constants and experimental frequencies as experimental data and the best compromised force constants were determined as those reproducing both sets of data as closely as possible in the least squares sense [62]. But so far, the most successful and most widely used scaling procedure was the scaled quantum mechanical (SQM) approach proposed by Pulay et al. [2,60]. In their method all the diagonal force constants are separated into different groups according to their chemical type and a scale factor is assigned to each group and the geometric mean of the diagonal scale factors are used for the off-diagonal force constants. The scale factors are optimized by minimizing the weighted mean square deviation between the calculated and observed fundamental frequencies. An arithmetic mean rather than the geometric mean of the diagonal scale factors for the off-diagonal force constants were attempted by Hipps and Poshusta in their scaling scheme [61]. More recently several other simpler scaling schemes were found in the literature where a fixed set of scale factors were used for every molecule [63,64] e.g. a scale factor of 0.9 for stretchings, 0.8 for bendings and their respective geometric mean for the coupling force constants was proposed by Durig et al. [64]. In all these scaling procedures the diagonal force constants are modified by using different scale factors while the off-diagonal force constants may be left unaltered or scaled down in some average manner. Since each force constant is physically distinct, it is more realistic to think that each force constant is associated with its own scale factor. Besides, the least squares method need not converge all the time, specially when the parameters are many and do not lead to a unique assignment, specially in less symmetric molecules. Goddard et al. for the first time proposed a different scheme of evaluating the force constants in the cartesian space from the experimental frequencies to use in their molecular mechanical studies [65]. Very recently Vijay and Sathyanarayana proposed their RECOVERS (recovery in the eigenvector space) procedure. This procedure uses a computationally simple scheme where the ab initio force constants are modified in a single step by the direct use of experimental eigenvalues of vibrational secular equation in the ab initio calculated eigenvector space. This method works well if the assignments are correct. However, it does not retain the sign of the ab initio force constants.

In this thesis we propose a new way of scaling the ab initio force constants and show

its applicability in the evaluation of reliable force constants and also in the theoretical prediction of vibrational spectra. The aim of this work is to present the methodology for scaling of *ab initio* force constants and compare its performance with the existing methods. As a result, we have chosen few very well studied systems like acrolein, benzene, naphthalene etc. for which earlier SQM results are available.

Secondly, a set of amino acids and a small dipeptide are chosen to show how this methodology can be extended to these systems to obtain a reliable theoretical force fields for these less symmetric molecules as an aid to determination of the force field parameters for molecular mechanics or molecular dynamics simulation of large biologically important molecules. Amino acids, being the building block of biologically active compounds are of special interest in both biological and structural chemistry. Amino acids exist as zwitterions in the condensed phase, whereas isolated molecules exhibit a neutral structure. While the zwitterionic structure is accessible via X-ray methods, the structure determination of neutral form poses severe experimental problems, since amino acids usually decompose before melting. As a result, so far the gas phase vibrational frequencies of amino acids are limited to glycine only. Any fitting or scaling procedure will perform well only when the *ab initio* model can reasonably mimic the gross features of experimental spectra. Since the *ab initio* calculations are mostly performed on isolated molecules, the best compromise between the theory and experiment is possible with gas phase vibrational data. The presence of intermolecular forces in the solid and solution phase leads to shift in the frequencies from the isolated molecular spectra. Thus, a judicious choice of the level of calculation or an improvement of the *ab initio* isolated model itself to account for this intermolecular effects, are very often needed to reproduce the experimental solid or solution phase spectra with all the isotopic shifts for amino acids [67]. Onsager reaction field approach of using a dielectric continuum is attempted to include the intermolecular H-bonding effects. A brief outline of the thesis is discussed in the next section.

## 1.1 Outline of the Thesis

The thesis has been arranged in the following manner:

In chapter 2, a brief discussion of the theory underlying *ab initio* force field calculations

are presented. In chapter 3, The newly developed scaling procedure is described in detail and testing of the present methodology is discussed with the examples of benzene, pyridine, acrolein and benzaldehyde. Benzene is used to compare the reliability of the force constants generated by the present methodology with that of Ozkabak and Goodman [3]. In chapter 4, the studies of naphthalene and anthracene in the light of transferability of scale factors between structurally related molecules are discussed in detail. In chapter 5, conformational and vibrational analysis of glycine hydrochloride and glycyglycine hydrochloride along with a theoretical prediction of the latter one from the former by the transfer of scale factors are discussed. In chapter 6, results of the calculations on cysteine and serine hydrochloride and a theoretical prediction of them from glycine hydrochloride and ethanethiol and ethanol respectively are discussed. Chapter 7, deals with glycine zwitterion. We explicitly show in this chapter that the isolated ab initio model fails to mimic the experimental spectra properly and incorporation of solvent effect can only improve the model. A set of non-redundant scale factors are obtained for solvated glycine zwitterion. In chapter 8, we use the same strategy as in glycine zwitterion to model the experimental spectra of alanine followed by a theoretical prediction of the vibrational spectra of cysteine and serine zwitterions using the alanine scale factors. Conclusions and future scope of the present work is discussed in chapter 9.

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# Chapter 2

## Methodology

The literature on ab initio calculations and normal coordinate analysis is vast and extensive. Hence this chapter does not purport to be a review of these methods. A flavour of the various theories and nuances underlying these methods are however presented in this chapter. Detailed description of these methods is given in references [1-19].

### 2.1 Ab Initio Methods

The Hamiltonian of a molecule consisting of N electrons and M nuclei in atomic units is -

$$\hat{H} = - \sum_{\alpha=1}^M \frac{1}{2m_{\alpha}} \nabla_{\alpha}^2 - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{\alpha=1}^M \frac{Z_{\alpha}}{r_{i\alpha}} + \sum_{\beta>\alpha} \sum_{\alpha} \frac{Z_{\alpha}Z_{\beta}}{r_{\alpha\beta}} + \sum_{j>i} \sum_i \frac{1}{r_{ij}} \quad (2.1)$$

where  $m_{\alpha}$  is the ratio of the mass of nucleus  $\alpha$  to the mass of an electron,  $Z_{\alpha}$  is the atomic number of nucleus  $\alpha$ ,  $r_{i\alpha}$  is the distance between electron i and nucleus  $\alpha$ ,  $r_{ij}$  is the distance between electron i and electron j and  $r_{\alpha\beta}$  is the distance between the nucleus  $\alpha$  and nucleus  $\beta$  respectively.

Within Born-Oppenheimer (B.O) approximation [20] one can consider that electrons in a molecule to be moving in the field of fixed nuclei and hence the kinetic energy of the nuclei can be neglected and the nuclear-nuclear repulsion can be considered to be a constant. Hence the Schrödinger equation for the electronic motion is -

$$\hat{H}_{el} \psi_{el} = E_{el} \psi_{el} \quad (2.2)$$

where,

$$\hat{H}_{el} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{\alpha=1}^M \frac{Z_{\alpha}}{r_{i\alpha}} + \sum_{j>i} \sum_i \frac{1}{r_{ij}} \quad (2.3)$$

The solution to Schrödinger equation involving the electronic Hamiltonian, is the electronic wave function,

$$\psi_{el} = \psi_{el}(r_i; r_{\alpha}) \quad (2.4)$$

which describes the motion of the electrons and explicitly depends on the electronic coordinates but depends parametrically on the nuclear coordinates, as does the electronic energy,

$$E_{el} = E_{el}(r_{\alpha}) \quad (2.5)$$

Thus the electronic energy including nuclear-nuclear repulsion for a fixed nuclei system must be

$$U = E_{el} + \sum_{\beta>\alpha} \sum_{\alpha} \frac{Z_{\alpha} Z_{\beta}}{r_{\alpha\beta}} \quad (2.6)$$

The vibration, rotation or translation of a molecule needs the solution to a nuclear Schrödinger equation

$$\hat{H}_{nuc} \phi_{nuc} = E_{tot} \phi_{nuc} \quad (2.7)$$

where  $E_{tot}$  is the total energy. The nuclear Hamiltonian for the motion of the nuclei in the average field of the electrons can be written as

$$\hat{H}_{nucl} = - \sum_{\alpha=1}^M \frac{1}{2m_{\alpha}} \nabla_{\alpha}^2 + U(r_{\alpha}) \quad (2.8)$$

Thus the total electronic energy including nuclear-nuclear repulsion constitutes a potential energy surface for the nuclear motion obtained by solving the electronic problem.

### 2.1.1 Hartree Fock Theory

The electronic problem is solved by considering a single Slater determinant as the ground state antisymmetric wave function in terms of molecular orbital  $\Psi_i$ ,

$$\Psi_i = \sum_{\mu=1}^N C_{\mu i} \Phi_{\mu} \quad (2.9)$$

where each molecular orbital is approximated as linear combination of finite set of basis functions and  $C_{\mu i}$  are the molecular orbital expansion coefficients.

The coefficients  $C_{\mu i}$  are chosen in such a way that the calculated total energy is minimum. This leads to the well known Roothan equations [21,22];

$$\sum_{\nu=1}^N (F_{\mu\nu} - \epsilon_i S_{\mu\nu}) C_{\nu i} = 0, \quad \mu = 1, 2, \dots, N; \quad i = 1, 2, \dots, N \quad (2.10)$$

where  $N$  is the total number of basis functions,  $\epsilon_i$  is the orbital energy of the  $i^{th}$  molecular orbital  $\Psi_i$ ,  $S_{\mu\nu} = \langle \Phi_\mu | \Phi_\nu \rangle$  are the overlap integrals and  $F_{\mu\nu}$  are the elements of the Fock matrix given by

$$F_{\mu\nu} = H_{\mu\nu}^{core} + \sum_{\lambda=1}^N \sum_{\sigma=1}^N P_{\lambda\sigma} \left[ (\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma) \right] \quad (2.11)$$

where

$$H_{\mu\nu}^{core} = \left\langle \Phi_\mu \left| -\frac{1}{2} \nabla^2 - \sum_{\alpha} V_{\alpha} \right| \Phi_\nu \right\rangle$$

is the one electron integral and

$$P_{\lambda\sigma} = 2 \sum_{i=1}^{OCC} C_{\lambda i}^* C_{\sigma i} \quad (2.12)$$

is the density matrix. The summation in equation (2.12) is over the occupied molecular orbitals only. Here  $P_{\lambda\sigma}$  represents the total electron population existing in the overlap region of the basis functions  $\Phi_\mu$  and  $\Phi_\nu$ . The factor 2 indicates that two electrons occupy each molecular orbital and the asterisk denotes complex conjugation. The electronic energy  $E_{el}$  can be expressed as

$$E_{el} = \frac{1}{2} \sum_{\mu=1}^N \sum_{\nu=1}^N P_{\mu\nu} (F_{\mu\nu} + H_{\mu\nu}^{core}) \quad (2.13)$$

The Roothan-Hall equation 2.10 is nonlinear, since the Fock matrix  $F_{\mu\nu}$  itself depends on the molecular orbital coefficients,  $C_{\mu i}$ , through the density matrix expression 2.12. Solution of it necessarily involves an iterative procedure. Since the resulting molecular orbitals are derived from their own effective potential, the technique is frequently called Self Consistent Field (SCF) theory. SCF calculations are known to give a good account of

the energy hypersurface only in the region close to the equilibrium molecular geometry. At larger deviations from the minima, the SCF potential curve starts to depart considerably from the "experimental" curve because of the neglect of electron correlation.

### 2.1.2 Electron Correlation

The inability of the Hartree Fock (HF) procedure to adequately account for the correlation of electron motion can be corrected by using more elaborate models comprising a multi-determinant wave function. Two techniques are widely used to incorporate the effect of electron correlation, one the configuration interaction [23] and the other the Moller Plesset perturbation theory [24]. The first method is variational but not size consistent but the second is size consistent but not variational. Variational implies that the calculated electronic energy should correspond to an upper bound to the energy that would result from the exact solution of the Schrödinger equation. Size consistency means that the method must give additive results when applied to an assembly of isolated molecules.

Thus the non-relativistic exact energy would be

$$E_{(exact)} = E_{(HF)} + E_{(correlation)} \quad (2.14)$$

#### Configuration Interaction (CI)

CI methods begin by noting that the exact wave function  $\Psi$  cannot be expressed as a single determinant, as HF theory assumes. CI proceeds by constructing other determinants by replacing one or more occupied orbitals within the HF determinant with virtual orbitals. A detailed account of CI and its applications are given in reference [25]. The size consistency of these methods can also be improved by coupled cluster methods [25]. Full CI is the most complete non-relativistic treatment of the molecular system possible, within the limitations imposed by the chosen basis set, though generally not computationally feasible. The rapid advancement of computer technology made it possible to consider yet upto one billion determinants full CI energy calculation of  $\text{Be}_2$  molecule so far [26].

#### Moller-Plesset Perturbation Theory (MP)

Since we have only employed the second order MP theory in our calculations, we briefly discuss the features of the second order Moller Plesset (MP2) calculations [27].



Perturbation theory is based upon dividing the Hamiltonian into two parts

$$H = H_0 + \lambda V \quad (2.15)$$

such that  $H_0$  is soluble exactly.  $\lambda V$  is a perturbation applied to  $H_0$ , a correction which is assumed to be small in comparison to it. The assumption that  $V$  is a small perturbation to  $H_0$  suggests that the perturbed wave function and the energy can be expressed in a power series in terms of  $\lambda$  according to the Rayleigh-Schrödinger perturbation theory [27].

In the MP theory  $H_0$  is defined as the sum of the one electron Fock operators.

$$H_0 = \sum_i F^i \quad (2.16)$$

The HF determinant and all other substituted determinants are eigenfunctions of  $H_0$  and we get

$$H_0 \Psi_s = E_s \Psi_s \quad (2.17)$$

where  $\Psi_s$  are the unperturbed functions representing all possible Slater determinants formed from  $n$  different spin orbitals.

When  $\Psi^{(0)}$  denotes the ground state, its energy is simply the sum of the orbital energies

$$E^{(0)} = \left\langle \Psi^{(0)} \left| \sum_i F^i \right| \Psi^{(0)} \right\rangle = \sum_i \epsilon_i \quad (2.18)$$

The first order correction to the energy is given by

$$E^{(1)} = \left\langle \Psi^{(0)} \left| V \right| \Psi^{(0)} \right\rangle \quad (2.19)$$

Adding  $E^{(0)}$  and  $E^{(1)}$  yields the HF energy (since  $H_0 + V$  is the full HF Hamiltonian).

$$E^{(0)} + E^{(1)} = \left\langle \Psi^{(0)} \left| (H_0 + V) \right| \Psi^{(0)} \right\rangle = E^{(HF)} \quad (2.20)$$

Thus the first order term does not incorporate any correction to the HF approximation.

The second order correction to the energy is given by

$$E^{(2)} = \left\langle \Psi^{(0)} \left| V \right| \Psi^{(1)} \right\rangle \quad (2.21)$$

where  $\Psi^{(1)}$  is a linear combination of substituted determinantal wave functions

$$\Psi^{(1)} = \sum_s a_s \Psi_s \quad (2.22)$$

Perturbation theory gives the following expression for  $\Psi^{(1)}$

$$\Psi^{(1)} = \sum_s \left[ \frac{\langle \Psi_s | V | \Psi^{(0)} \rangle}{E^{(0)} - E_s} \right] \Psi_s \quad (2.23)$$

The second order energy correction can be written as [27]

$$E^{(2)} = - \sum_s \frac{|\langle \Psi^{(0)} | V | \Psi_s \rangle|^2}{E_s - E^{(0)}} \quad (2.24)$$

Thus, the value  $E^{(2)}$ , the first correction to the HF energy, will always be negative. The numerator will be nonzero only for double substitutions. Single substitutions are known to make this expression zero by Brillouin's theorem.

### 2.1.3 Basis Sets

Basis sets play an important role in the evaluation of the energies. A limiting HF treatment would involve an infinite number of basis functions. This is clearly impractical since the computational expense of HF molecular orbital calculation is formally proportional to the fourth power of the total number of basis functions. Therefore the ultimate choice of basis set size depends on a compromise between accuracy and cost. For computational utilities it is desirable to use gaussian basis functions  $g(r)$ , [28] where  $r$  is the position vector  $(x,y,z)$ . Excellent reviews exist on basis sets [19,29-32] and their limitations. Methods to construct new basis sets are described in reference [19]. We discuss here briefly the salient features of different basis sets.

#### Minimal Basis Set

The STO-3G minimal basis set was developed by Pople and co workers for first row elements [33]. It was later extended to the second row [34], third row [35] and fourth row [36] elements. It has also been applied to first and second row transition metals [37]. It is characterized by its small size and effectiveness in predicting geometries [38]. The remarkable agreement of the STO-3G geometries to the experimental geometries is due to the large basis set superposition error which helps cancel other defects to produce

reasonable bond parameters. It can be expressed as

$$\Phi_{nl}(\zeta = 1, r) = \sum_{k=1}^3 d_{nl,k} g_l(\alpha_n, k, r) \quad (2.25)$$

where the subscripts  $n$  and  $l$  define the specific principal and angular quantum numbers,  $g_l$ s are the normalized gaussian functions,  $\alpha_n$ s are the gaussian exponents and  $d_{nl,k}$ s are the linear expansion coefficients. The values of  $\alpha$  are determined by minimizing the error in the fit of the gaussian expansion to the exact Slater orbitals. The STO-3G basis description of conjugated systems and polar molecules is far from satisfactory. This is due to the fact that all the elements of a single row of the periodic table have the same description.

### Split Valence Basis Set

A basis set formed by doubling or tripling all functions of the minimal representation is usually termed a double-zeta or triple-zeta basis set. An even simpler extension of the minimal basis set is to double or triple only the number of basis functions representing the valence region and is known as split valence basis set. These split valence basis sets are a compromise between the speed obtained using a minimal basis and the accuracy of the larger ones. The 4-21G [38] basis is extremely suitable for geometry optimizations utilizing the analytic gradients. A reduced version of the 4-21G basis set, the 3-21G basis set [39,40] is also used in routine calculations. The characteristics of both the basis sets are similar. The 4-31G and 6-31G bases are generated by increasing the number of primitives devoted to the core and first valence electron functions. The 4-31G [41] and 6-31G [42] bases improve upon 3-21G energetics at the expense of increased computer time.

### Polarization Basis Set

Polarization functions are needed for the description of the highly polar molecules and of systems incorporating small strained rings. These systems require that some allowance be made for the possibility of non-uniform displacement of charges away from the atomic centers. Adding all the five components of a cartesian d function to the first row elements of 6-31G basis set gives the 6-31G\* basis set. Further addition of p functions to the hydrogen atoms results in the 6-31G\*\* basis set. These basis sets are first proposed by Hariharan and Pople [43] for the first row elements and later extended to the second

row elements [44]. A larger polarization basis set, 6-311G\*\* has been formulated for the first row elements [45]. It comprises an inner core of six s type gaussians and an outer (valence) region, which has been split into three parts, represented by three, one and one primitives, respectively. This basis set is supplemented by a single set of five /six d-type gaussian functions for first row atoms and a single set of uncontracted p-type gaussians for hydrogen.

### Diffused Basis Set

This set of functions are needed for species with significant electron density far removed from the nuclear center. Such species involve anions for which the extra electron is only weakly bound and hence is needed to include in the basis representation one or more sets of highly diffuse functions [46]. The 3-21+G and 6-31+G\* basis sets for the first row elements and 3-21+G, 3-21+G\* and 6-31+G\* basis sets for second row elements [47] are constructed from the underlying 3-21G, 3-21G\* and 6-31G\* representations by the addition of a single set of diffuse gaussian s and p-type functions. The higher 6-31++G\* and 6-31++G\*\* basis sets include an extra diffuse function to the hydrogen of the corresponding 6-31+G\* and 6-31++G\* basis sets.

### 2.1.4 Reaction Field Model of Solvation

In the vibrational analysis of amino acid zwitterions the Onsager reaction field model is used in this thesis. A brief outline of this method is presented here.

#### Onsager Reaction Field Model

In this model [48] the solute is placed in a cavity (usually spherical) immersed in a continuum medium with a dielectric constant  $\epsilon$  [49]. A dipole in the molecule will induce a dipole in the medium and the electric field applied to the solute by the solvent (reaction) dipole will in turn interact with the molecular dipole leading to a net stabilization. In the MO theory, the electrostatic solvent effect may be taken as an additional term  $H_1$  in the Hamiltonian of the isolated molecule  $H_0$  giving,

$$H_{rf} = H_0 + H_1 \quad (2.26)$$

The perturbation term ( $H_1$ ) describes the coupling between the molecular dipole operator ( $\hat{\mu}$ ) and the reaction field,  $\vec{R}$

$$H_1 = -\hat{\mu}\vec{R} \quad (2.27)$$

The reaction (electric) field,  $\vec{R}$ , is proportional to the molecular dipole moment,  $\vec{\mu}$

$$\vec{R} = g\vec{\mu} \quad (2.28)$$

The proportionality constant  $g$ , which gives the strength of the reaction field depends on the dielectric constant of the medium  $\epsilon$  [50], and on the radius of the spherical cavity  $a_0$ . The value of  $g$  is given by the equation

$$g = \frac{2(\epsilon - 1)}{(2\epsilon - 1)a_0^3} \quad (2.29)$$

For the case of a self-consistent field wave function the effects of the reaction field can be incorporated as an additional term in the Fock matrix as

$$F_{\lambda\sigma} = F_{\lambda\sigma}^0 - g\vec{\mu} \langle \phi_\lambda | \hat{\mu} | \phi_\sigma \rangle \quad (2.30)$$

where  $\phi_\lambda$  and  $\phi_\sigma$  are basis functions. When the solvent polarization is included, the energy of the system is given by

$$E = \langle \Psi | H_0 | \Psi \rangle - \frac{1}{2}\vec{\mu}\vec{R} \quad (2.31)$$

where  $\Psi$  is the full wave function of the molecule.

### 2.1.5 Force Constants

The evaluation of force fields is one of the foci of this thesis. The starting point of all force field evaluations is the harmonic approximation.

#### Harmonic Approximation

Within the harmonic approximation, the nuclear potential  $V(R_1, \dots, R_M)$  is expressed as the quadratic terms in a power series expansion of the total energy  $E(R_1, \dots, R_M)$  about the equilibrium position,

$$E = E(X_1^o, \dots, X_{3M}^o) + \sum_{i=1}^{3M} \frac{\partial E}{\partial X_i} \Big|_o \Delta X_i + \frac{1}{2} \sum_{j=1}^{3M} \frac{\partial^2 E}{\partial X_i \partial X_j} \Big|_o \Delta X_i \Delta X_j + \dots \quad (2.32)$$

where  $X_1, X_2, \dots, X_{3M}$  are the cartesian coordinates of the  $M$  nuclei. The first term in the R. H. S of equation (2.32) is constant for all  $E_{nuc}$  and hence can be ignored. Since  $E$  is a minimum at the equilibrium geometry

$$\frac{\partial E}{\partial X_i} \big|_o = 0 \quad (2.33)$$

Hence the second term in equation (2.32) vanishes. If all terms of order higher than two are neglected, the potential is a quadratic function of the nuclear displacements  $\Delta X_i$

$$E(X_1, \dots, X_{3M}) \equiv \frac{1}{2} \sum_{j=1}^{3M} F_{ij} \Delta X_i \Delta X_j \quad (2.34)$$

where the force constants  $F_{ij}$  are given by

$$F_{ij} = \frac{\partial^2 E}{\partial X_i \partial X_j} \big|_o \quad (2.35)$$

Equation (2.34) represents the harmonic approximation. For small displacements about the equilibrium position, equation (2.34) is valid, but it is not accurate for large distortions.

A transformation to mass weighted cartesian coordinates  $\rho_i = (m_i)^{\frac{1}{2}} \Delta X_i$  followed by rotation of the coordinates to coincide with the principal axes of the quadratic form in equation (2.34) gives an expression for  $V$  containing only squared terms.

$$V = \frac{1}{2} \sum_{i=1}^{3M} \lambda_i Q_i^2 \quad (2.36)$$

where  $Q_i$  are coordinates relative to the principal axes and hence called "normal coordinates". As a result of these transformations equation (2.34) which depends on  $3M$  variables separates into  $3M$  equations, each depending upon a single  $Q_i$ . Further each of these is a harmonic oscillator equation with eigen value  $\lambda_i$ .

For non linear molecules six of the  $\lambda_i$ s corresponding to three translational and three rotational motions of the entire molecule are zero. These six  $\lambda_i$ s can be removed by working in a coordinate system having the origin at the center of mass and rotating with the molecule. The remaining  $3M-6$  degrees of freedom are usually specified by internal coordinates such as bond lengths, bond angles and dihedral angles. As a result, fewer force constants need to be evaluated and those that are evaluated have physical interpretation.

Though the harmonic approximation is good enough for most vibrational calculations, recent studies indicate that the inclusion of anharmonicity leads to a better agreement with the experimental frequencies. But these are limited to small molecules [51] and extension of the anharmonic treatment to a relatively large system of chemists' interest is yet in its infancy.

### Anharmonicity

Most of the vibrational calculations to date have used the harmonic approximation of equation (2.34) but with the progress in ab initio calculations, cubic and quartic force constants can now be evaluated. These are the third and fourth order terms dropped from equation (2.34). The inclusion of them in equation (2.34) allows the possibility of including anharmonicity in ab initio treatments. Perturbation theory yields the following formula for anharmonicity [17].

$$\chi_{rr} = \frac{1}{16} \Phi_{rrrr} - \frac{1}{16} \sum_s \Phi_{rrs}^2 \frac{[8\omega_r^2 - 3\omega_s^2]}{\omega_s(4\omega_r^2 - \omega_s^2)} \quad (2.37)$$

Equation (2.37) contains the quadratic, diagonal quartic and semi diagonal cubic force constants. The  $\omega_k$  are the harmonic frequencies. The evaluation of the quartic force constant  $\Phi_{rrrr}$  is given in reference [52]. A detailed treatment of anharmonicity and its inclusion in force field calculations is given in references [53-55].

## 2.2 Transformation of Force Constants

The quantum mechanically calculated ab initio force constants are generally derived with respect to the cartesian coordinates. Transformation of these cartesian force constants to internal coordinates helps to interpret the results within the GF matrix formalism of the vibrational problem by Wilson [11].

In cartesian coordinates the diagonal force constants are not necessarily dominant and the useful concept of partitioning the potential into dominant diagonal versus less important coupling terms is lost. The force constants in internal coordinates are physically meaningful and are easy to compare and transfer between structurally related molecules.

The basic types of internal coordinates bond stretching, valence angle bending, out of plane bending and torsions proposed by Wilson, Decius and Cross [11] are generally accepted, although there are variations in handling of redundancy and symmetry. A set of non-redundant internal coordinates were recommended by Pulay et al. as an alternative [18]. These coordinates are local, i.e., use of local coordinates which extend over a few neighbouring atoms only, based on local symmetry. These non-redundant local coordinate facilitate the transfer of force constants from one molecule to the other.

The main bottleneck in the conversion of the cartesian force constants to internal force constants is that the force field matrix in cartesian coordinates spans a  $3N$  dimensional space,  $N$  being the number of atoms, while the number of non-redundant internal coordinates is only  $3N-6$  (or  $3N-5$  for linear molecules). The transformation from cartesian to internal coordinates can be described as follows [56].<sup>32</sup> The potential energy surface of a given state can be described both in cartesian coordinates and in internal coordinates as

$$E(x) = E_o(x) + g.x + 0.5.x^\dagger.H.x \dots \quad (2.38)$$

$$E(q) = E_o(q) + f.q + 0.5.q^\dagger.F.q \dots \quad (2.39)$$

where  $q$  is the internal coordinate vector,  $x$  is the cartesian vector,  $g$  and  $f$  are the gradients,  $H$  and  $F$  are the second derivative matrices in the two frameworks. Wilson's  $B$  matrix transforms cartesian into internal coordinates, as  $q=Bx$  [11]<sup>33</sup> and from 2.38 and 2.39 we get

$$F = B^{-1\dagger}.H.B^{-1} \quad (2.40)$$

Since  $B$  is a rectangular matrix, to invert it, it is necessary to use the notion of a generalized inverse matrix.

$$B^{-1\dagger} = (BB^\dagger)^{-1}.B \quad (2.41)$$

However  $BB^\dagger$  could be singular so that the conversion is always not possible. The symmetric  $G$  is non-singular [57]<sup>33</sup> and can be inverted. If  $A$  is the inverse of  $B$  and  $M$  is the atomic mass diagonal matrix of order  $3N \times 3N$  then we have

$$AB = E$$

$$AB.M^{-1}.B^\dagger = E.M^{-1}.B^\dagger$$



$$AG = M^{-1}B^\dagger$$

$$A = M^{-1}B^\dagger G^{-1}$$

as given in [58]. Translating to local symmetry,

$$A_{loc}B_{loc} = E \quad \text{where } B_{loc} = U_{loc}B$$

Postmultiplying  $M^{-1}B_{loc}^\dagger$  on both sides we have

$$A_{loc}B_{loc}M^{-1}B_{loc}^\dagger = M^{-1}B_{loc}^\dagger$$

$$A_{loc}G_{loc} = M^{-1}B_{loc}^\dagger$$

$$A_{loc} = M^{-1}B_{loc}^\dagger G_{loc}^{-1}$$

From equation 2.40,  $F_{loc} = A_{loc}^\dagger F_{cart} A_{loc}$

Here  $A_{loc}$ ,  $G_{loc}$ ,  $F_{loc}$  are the local symmetric A, G and F matrices respectively.  $U_{loc}$  is the transformation matrix which contains the description of the local symmetry coordinates in terms of internal coordinates.

The local symmetric force constants could be transformed to the symmetric force constants easily using

$$F_{sym} = U_{ortho} F_{loc} U_{ortho}^\dagger \quad (2.42)$$

where  $U_{ortho}$  is the orthogonal transformation matrix.

## 2.3 Computational Details

All ab initio calculations were done using Gaussian 90-94 [59] and GAMESS [60] suit of programs installed on Convex-C220, HP-9000/735 and Dec-Alpha computer systems. The normal coordinate analyses were done based on the modified version of the programs of Schachtschneider [61]. The conversion of cartesian force constants to local symmetric force constants were done using a modified version of the program VECEIG kindly provided by Dr. Amarendra Vijay and Professor D. N. Satyanarayana.

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## Chapter 3

# Interpretation and Accurate Prediction of Vibrational Spectra - A Modification to Scaled Quantum Mechanical Approach

An accurate knowledge of molecular force fields is essential in the prediction and interpretation of vibrational spectra and also in molecular mechanics and dynamics calculations [1-4]. Attempts to deduce molecular force fields from spectral data alone have not been successful so far for molecules containing more than a few atoms [1,2]. As the number of atoms increases, the number of force constants to be determined becomes more than the experimentally available frequencies and multiple solutions become a problem. Ab initio molecular orbital methods offer an attractive alternative to resolve these problems. However, finite basis set and neglect of electron correlation in the HF procedure overestimates most of the harmonic force constants by 10-30% [1]. Although recent methods like CCSD(T) and CASS are capable of yielding more accurate harmonic force constants compared to Hartree-Fock theory, still produce errors compared to the experimental values [5]. These methods can not be applied on a routine basis to medium sized molecules of 5-30 atoms which are of chemists' interest. Even when accurate harmonic force constants become available, for prediction of experimental frequencies we need anharmonic force constants which involve the evaluation of cubic and quartic force constants. So it appears that, as pointed out by Pulay, the realistic solution is to stay at the Hartree Fock level of theory and make a correction for the systematic errors by means of some scaling procedure [6]. Of the different scaling procedures, the scaled quantum mechanical(SQM)

approach of Pulay appears to be the most successful one [1]. However, SQM approach uses least squares procedure to optimize a small number of scale factors as a measure of the systematic errors in the ab initio calculation. Since each force constant is physically distinct, it is more realistic to think that each force constant is associated with its own scale factor. Besides, the least-squares method need not converge all the time, specially when the parameters are many and do not lead to a unique assignment [7]. In this chapter we give a novel numerical procedure which overcomes these difficulties.

In the first part of the chapter a detailed description of the methodology and its theoretical justification is presented. The advantages of the present methodology over the existing ones are listed. In the second part the performance of the method is demonstrated by using acrolein, benzene, pyridine and benzaldehyde as examples.

### 3.1 Methodology

Evaluation of force constants of a molecule involves the solution of the inverse eigenvalue equation  $GFL=LA$  where  $F$  is the force constant matrix,  $A$  the frequency matrix ( $\lambda_i=4\pi^2\nu_i^2$ ),  $G$  the Wilson's  $G$  matrix and  $L$  the eigenvector matrix describing the normal modes [8]. Usually  $F$  is varied and  $A$  is calculated until  $A$  matches with the experimental frequencies. As long as we are modifying the force constants to obtain the frequencies of the molecule, the method would involve intuition and an element of arbitrariness depending on how we modify the  $F$  matrix elements. To get around this difficulty we modify the frequencies in the proposed method, so that the force constants automatically get refined in the right direction to reproduce the experimental frequencies.

The method involves the following steps:

- (1) Diagonalize  $G$  matrix:  $G=DFD^t$
- (2) Form  $W_1=DF^{1/2}$  and  $W_2=DF^{-1/2}$
- iter=0
- (3) Start  $F_1$ ; iter=iter+1



- (4) Form  $W_1^t F_1 W_1 = H_1$   
 (5) Diagonalize  $H_1$  matrix:  $H_1 = C \Lambda_1 C^t$   
 (6) Form  $L = W_1 C$  and normalize  $C$  such that  $LL^t = G$   
 (7) Modify  $\Lambda_1$  with a small correction  $\Delta\Lambda$  given by  $\Delta\Lambda = (\Lambda_{exp} - \Lambda_1)(iter-1)/Niter$   
 where Niter is the total number of iterations (we used Niter=1000);

$$\Lambda_2 = \Lambda_1 + \Delta\Lambda$$

- (8) Form  $H_2 = C \Lambda_2 C^t$   
 (9)  $F_2 = W_2 H_2 W_2^t$

The  $F_2$  elements are averaged to retain the symmetry. This means that the force constants which are equal in the unscaled  $F$  matrix will be made equal. For example, benzene in-plane  $F$  matrix contains only 26 different numbers as described in references 2 and 8.

- (10) Replace  $F_1$  by  $F_2$  and go to step 3.

After going through the cycle Niter times  $\Lambda_{calc.}$  will be equal to  $\Lambda_{exp}$  and we will have the refined  $F$  which will reproduce the experimental frequencies. The frequencies of many isotopically substituted molecules could be fitted, using the fact that the  $F$  matrix is the same for the different isotopomers. In each cycle  $F_2$  is calculated for each isotopic species and an average  $F_2$  is used as  $F_1$  in the next cycle.

To get the scale factors in the desired range we can define values for the lowest and the highest permitted scale factor. After step 9, the  $F_2$  elements are compared with the unscaled ab initio force constants. If the scale factors are between the allowed values they are updated; otherwise the value from the last cycle is retained. The flowchart of the algorithm is given in Figure 3.1.

### Theoretical Justification

The theoretical justification for the above procedure could be given based on perturbation theory. Each step in the iteration is a small perturbation. The Wilson's GF matrix

equation can be written in terms of time independent Schrödinger equation [8] -

$$H_0\Psi_0 = E_0\Psi_0 \quad (3.1)$$

where,  $GF_1=H_0$ ,  $L_1=\Psi_0$  and  $\Lambda_1=E_0$

When a small perturbation ( $\Delta F$ ) is applied (since each step is a small perturbation),  $H'=G\Delta F$  and the first order correction is given by

$$E_1 = \langle \Psi_0 | H' | \Psi_0 \rangle = \Delta\Lambda = (L_1)^{-1}G\Delta F(L_1) \quad (3.2)$$

Since  $G=L_1L_1^t$ ,

$$\Delta\Lambda = (L_1)^{-1}L_1L_1^t\Delta F(L_1) = L_1^t\Delta FL_1 \quad (3.3)$$

As long as the perturbation  $\Delta F$  is small compared to  $F$ , the perturbation theory is expected to give valid results. Our goal is to retain the characteristics of the ab initio force field *as far as possible* when making the correction for the systematic over-estimation of the force constants. So we choose  $\Delta F$  in such a way that  $\Delta\Lambda$  is diagonal. This means  $L_1$  is an eigenfunction of  $H'$  also and so the ab initio characteristics are retained. Since we do not calculate  $\Delta\Lambda$  from  $\Delta F$  but calculate only  $\Delta F$  from  $\Delta\Lambda$  choosing  $\Delta F$  such that  $\Delta\Lambda$  is diagonal is not a problem.

From  $GF_1L_1=L_1\Lambda_1$  and  $G=L_1L_1^t$ , it can be easily shown that

$$\Lambda_1 = L_1^tF_1L_1 \quad (3.4)$$

In each iteration  $\Delta\Lambda$  ( $\lambda_{exp}-\lambda_1$  is negative for overestimated ab initio frequencies) is added to the previous calculated frequency to get the modified frequency. Since,  $\Lambda_2=\Lambda_1+\Delta\Lambda$ , combining 3.3 and 3.4 we get

$$\Lambda_2 = L_1^t(F_1 + \Delta F)L_1 \quad (3.5)$$

or,

$$\Lambda_2 = L_1^tF_2L_1 \quad (3.6)$$

which leads to

$$F_2 = (L_1^t)^{-1}\Lambda_2(L_1)^{-1} \quad (3.7)$$

Since,  $L_1=W_1C$ , we get

$$F_2 = [(W_1C)^t]^{-1}\Lambda_2[W_1C]^{-1} = (D\Gamma^{-1/2})(C\Lambda_2C^t)(D\Gamma^{-1/2})^t = (D\Gamma^{-1/2})H_2(D\Gamma^{-1/2})^t \quad (3.8)$$

from which we get,

$$F_2 = W_2 H_2 W_2' \quad (3.9)$$

The justification for averaging the  $F_2$  elements according to symmetry comes from the fact that the  $F$  matrix always should reflect the symmetry of the molecule. For example in  $C_6H_6$ , all C-C stretching force constants should be equal. Because of the numerical procedure of calculating  $F_2$  ( $F_2 = W_2 H_2 W_2'$ ), the C-C force constants will not agree in all decimal places, although they are all close. To impose the symmetry constraint, we average all the C-C stretching force constants so that they are equal in all decimal places.

Since  $F_2$  elements are averaged to retain the symmetry and only those elements which give the right scale factors are updated, in the next cycle many of the new  $F_1$  elements will be different from the corresponding  $F_2$  elements obtained using equation 3.9. If the perturbation is small, this difference will be very small reproducing the same calculated  $\Lambda_2$ . However, since the  $\Delta F$  is different from that of  $F_2$  obtained from equation 3.9,  $\Delta \Lambda = L_1' \Delta F L_1$  is not diagonal. As a result the eigenvectors of the last cycle will get mixed up in the present cycle.

Using first order perturbation theory

$$\Psi_n^{(1)} = \sum_{k \neq n} \frac{\langle \Psi_k^0 | H' | \Psi_n^0 \rangle}{E_n^0 - E_k^0} \Psi_k^0 \quad (3.10)$$

where,  $\langle \Psi_k^0 | H' | \Psi_n^0 \rangle$  is very small in each step as explained above. Hence only when  $\lambda_n - \lambda_k$  is small, the eigenvectors will get mixed. This means that when two frequencies are close, their potential energy distributions will get mixed up and in the worst case, the assignments will get interchanged. Since the ab initio calculation is for a non-interacting isolated molecule whereas the *real experimental frequencies are from 'interacting environment'*, when the frequencies are close, a certain amount of mixing or interchange of assignments could be justified. This happens most of the time among the  $CH_3$  stretching frequencies, where a certain amount of mixing or exchange between the assignments are permitted. It is to be noted that the mixing among degenerate modes does not create any problem.

To investigate the performance of the present methodology to obtain corrections for the over-estimation of the force constants we used benzene as the test case. The experimentally determined force constants of Ozkabak and Goodman from reference [2] are used to

obtain the harmonic frequencies of benzene. These calculated frequencies are used as 'simulated experimental frequencies' and the force constants are randomly over-estimated by multiplying with a scale factor between 1/0.6 and 1.0. These over-estimated force constants are fitted to the simulated frequencies and the results are given in Table-3.1. As indicated in the Table, with one decimal accuracy in the harmonic frequencies the 2x2 blocks of force constants are reproduced. When the accuracy is  $\pm 1\text{cm}^{-1}$ , the  $A_{1g}$  block off-diagonal element is off by 8%. In 3x3 block even one decimal accuracy in frequencies does not reproduce OG values for  $F_{18,20}$  and  $F_{19,20}$ . This clearly proves that the true force constants could not be obtained from frequency data alone for 3x3 blocks and higher. However, with an error limit of  $\pm 1\text{cm}^{-1}$  which is the accuracy for the experimental frequencies, the numbers are very close to the real ones and represents a reliable force field. It appears that if the ab initio force field is the right one except for the over-estimation, the present methodology produces a satisfactory set of force constants when sufficient number of frequencies are available.

The choice of the number of iterations only requires that  $\Delta\Lambda$  is small compared to  $\Lambda$  so that the perturbation  $G\Delta F$  is small. We tested with Niter=100 to Niter=1500 in steps of 100. It appears that after Niter=500, the results do not change significantly, at least for the molecules we have tested. If there are sufficient number of experimental frequencies as long as  $\Delta\Lambda$  is small, the results are expected to be largely independent of Niter. When there are not enough experimental frequencies, for example, when only one isotopomer experimental frequencies are available, the final force constants are good approximations to the true values and different Niter values may not produce force constants which agree in all decimals although they will be close to each other (see the pyridine results described latter). However, since the present method offers a systematic procedure, the force constants from two structurally related molecules fitted with same Niter could be compared or scale factors could be transferred among them to obtain good results. Similar considerations apply to the lower and upper limit of the scale factors, which is based on the assumption that the errors are systematic.

If ab initio theory is a good model for the real system then the assignments are reasonable if the final potential energy distributions (PED)s are close to that of the original

unscaled PEDs. If the assignment is incorrect, the fitted frequency will be very much off from the experimental frequency and the PEDs will be unacceptable.

The Advantages of the Current Procedure are:

- (1) We get a set of scale factors which could be used to study the trends related to structural variations and for predicting the frequencies of the structurally related molecules.
- (2) There is an in-built check to detect the mathematical inconsistencies arising from a wrong assignment by giving fitted frequencies which are very different from the experimental numbers.
- (3) The effort needed to fit the frequencies of one isotopomer is almost the same as fitting the frequencies of any number of isotopically substituted molecules and very much less than that of the least squares method.

This method could be used for other inverse eigenvalue problems, for example in NMR spectroscopy [9]. Another interesting application could be in obtaining a good estimate for electron correlation by scaling the Fock matrix of the Hartree-Fock theory.

The normal coordinate analyses are done with a modified version of the UMAT program [10].

## 3.2 Results

### 3.2.1 Interpretation of Vibrational Spectra

#### Acrolein

To see how this method performs compared to the known SQM cases, we calculated the fitted force constants, frequencies and potential energy distributions of all the molecules described in reference 1. The results for a representative case, acrolein-d<sub>0</sub> and d<sub>1</sub> are shown in Table-3.2. We used the same scale factor limits of 0.7 and 1.0. The agreement with the experimental frequencies are almost quantitative. The average deviations of all the frequencies of acrolein-h<sub>4</sub> and acrolein-d<sub>1</sub> is only 2.3 cm<sup>-1</sup>. Since, the gas phase

experimental numbers are used, the agreement is so excellent and the final fitted PEDs exactly reproduce the ab initio unscaled PEDs, as expected. In almost all the bands, our calculated numbers show an improvement over the earlier SQM results [1].

## Benzene

The first demonstration of benzene potential surface was due to the pioneering work of Wilson as early as 1934, using only six force constants [11]. After that several papers appeared on the generation of the force field and reliable vibrational frequency assignments for benzene [12-17]. But the real improvement in the frequency data came in the last decade with the introduction of new experimental techniques [18-20]. Accurate measurement of the inactive fundamentals in IR and Raman spectra and unambiguous identification of  $A_{2g}$  and  $B_{1u}$  modes in lower symmetry isotopically labelled benzenes had become possible due to the invention of the two-photon spectroscopy [19,20]. So far the most reliable and detailed analysis of benzene ground state vibrational force field available was that of OG [2]. On the other hand, there was a good deal of advancement in the theoretical force field of benzene through the analytic derivatives of the electronic energy at the HF and correlated level using the gradient algorithm of Pulay [21]. A reliable theoretical force field was first proposed by Pulay et al. by scaling the ab initio force constants using their SQM methodology [22]. HF and higher correlated level ab initio calculations were carried out by Guo and Karplus to obtain the benzene force constants for planar vibrations [23]. These theoretical force fields differ in some values especially in the off-diagonal force constants compared to the OG force field.

Since we start with the assumption that the ab initio force field is the right one except for the systematic errors, the multiple solution problem in the usual sense i.e. entirely different sets of force constants giving identical frequencies [24] does not arise although the different ways of scaling could produce different approximations to the *same* theoretical force field which are very similar to each other. After correcting the systematic errors by means of scaling what we get is the scaled ab initio force field.

All the 34 different scaled ab initio force constants of benzene obtained by fitting

the harmonic frequencies of the four  $D_6h$  isotopomers using five different basis sets (4-21G, 6-31G\*, 6-311G\*\*, 6-31++G\*\* at HF level and 6-311G\*\* at MP2 level) are shown in Table-3.3 along with the OG force field [2] and that of Pulay et al. [22]. Table-3.4 contains the corresponding scaled frequencies of benzene- $d_0$  along with the calculated harmonic frequencies of OG. Since, the calculated frequencies are almost same in all the different levels of calculation, the harmonic frequencies for all the three ( $C_6D_6$ ,  $^{13}C_6H_6$  and  $^{13}C_6D_6$ ,  $C_6H_6$  frequencies appear in Table-3.4) isotopes are shown in Table-3.5 only at HF/4-21G level. The force field is obtained by fitting the respective ab initio force constants to the most accurate OG experimental frequencies at the experimental geometry of benzene. The fitted force constants presented in Table-3.3 are nearly unique with respect to different levels of calculations and obviously appear as an improvement over the earlier theoretical force fields. The agreement with the experimental OG force field is very good in the diagonal force constants and in many of the off-diagonal force constants. But the discrepancy arises (mainly in the off-diagonal constants) at those places, where the ab initio model itself predict entirely different values including the sign. The scaling procedure retains the sign of the ab initio force constants. Such a difficulty cannot be resolved by merely scaling the force constants.

It is tempting to explain the scaled force constants of benzene given in Table-3.3 in the following way. In the one dimensional cases ( $A_{2g}, A_{2u}, E_{1g}$ ) only one frequency is needed and it gives a unique force constant. In 2x2 ( $A_{1g}, B_{1u}, B_{2u}, B_{2g}, E_{2u}$ ) we require at least three observed frequencies to get a unique set of force constants (3 equations and 3 unknowns). In 3x3 ( $E_{1u}$ ) we need 6 frequencies to make 6 equations with 6 unknown force constants. In 4x4 ( $E_{2g}$ ) we require 10 frequencies to solve for 10 force constants. The scaled force field is nearly identical in all blocks except for  $E_{2g}$  because sufficient number of frequencies are not available for exact solution in  $E_{2g}$ . Only 9 distinct frequencies are available when 10 are required for exact solution [24]. As a result the force field varies marginally for  $E_{2g}$  based on the starting F matrix. But unfortunately, 'uniqueness' does not imply 'accuracy' as shown in the methodology section. Some of the force constants are *very sensitive* to frequencies to the extent that their correct values could not be determined from *frequency data alone*. For example, in the 2x2 solutions,  $A_{1g}$  and  $B_{1u}$  off-diagonal

elements are different from that of OG although the OG numbers are reproduced when calculated frequencies from OG force constants are used as simulated experimental data with 3 decimal accuracy! Probably the 'uniqueness' is an 'accidental coincidence' due to the selection of range of scale factors for the different basis sets (see Table-3.3).

The question whether ab initio methods can produce the true force constants, however, cannot be answered at this point. Extended basis set calculations including correlation appears to disagree in some values with the experimental force field of OG. However, in *many* of the force constants the agreement with experimental force field is *quantitative* after scaling with the *present methodology*. Since experimental force field is available only for few small symmetric molecules, the scaled ab initio values appear to offer an attractive alternative.

### 3.2.2 Prediction of Vibrational Frequencies

#### Pyridine

Experimental vibrational spectra of pyridine in crystalline as well as matrix isolated form along with several deuterium substituted species are widely available in the literature [25-32]. Transferability of benzene force constants/scale factors to predict pyridine fundamentals had been attempted by several authors [6,33,34]. But so far the most successful study of this kind was done by Pulay et al. where they transferred the ab initio 4-21G scale factors of benzene to predict the pyridine spectra [6]. We obtained a set of scale factors of benzene-d<sub>0</sub> and d<sub>6</sub> individually and collectively at HF/4-21G level and used them to predict the frequencies of pyridine-d<sub>0</sub> and d<sub>5</sub> from ab initio force constants. No experimental numbers are used in prediction. For comparison we list the predicted values by the SQM method in Table-3.6. Table-3.6 clearly shows that the overall fitted frequencies are in better agreement compared to the individual ones, except for the C-H and C-D stretching frequencies. Since the associated anharmonicity is more in these modes, the individual fitted scale factors when transferred can produce better correction to the calculated frequencies compared to the overall fitted scale factors. Our predicted frequencies are in good agreement with the earlier predicted SQM frequencies which included



the cubic force constants also in the analysis.

### Benzaldehyde

As an additional test the same set of scale factors, as obtained by fitting benzene- $d_0$  individually to the experimental spectra, combined with scale factors of acetaldehyde- $d_0$  at 4-21G level are used to predict the frequencies of benzaldehyde- $d_0$  using ab initio force constants obtained at the same level of theory. The results are in excellent agreement with the experimental numbers [35] as shown in Table-3.7. The average error of the predicted frequencies is less than  $5.9\text{ cm}^{-1}$ . Larger deviations are found mainly in the  $3000\text{ cm}^{-1}$  (C-H stretching) region, which are highly anharmonic.

Internal coordinates of acetaldehyde and benzaldehyde, force constants of acrolein, benzaldehyde and scale factors of benzene and acetaldehyde are presented in Tables-3.8 to 3.15.

### 3.3 Conclusions

All the results presented in this study indicate that the present methodology of fitting the experimental frequencies to the ab initio force constants and transferring the scale factors from structurally related molecules to predict the fundamental frequencies offer an attractive solution to the vibrational spectral interpretation and prediction.

Step 1: Convert cartesian force constants obtained from the ab initio program to force constants in local symmetry coordinates. We refer to this F matrix as  $F_{ab}$

Step 2: Input: No. of isotopic species (nmol), masses (M), Wilson's B matrix (B), local U ( $U_{loc}$ ).

We used Niter = 1000 and a scale factor range of 0.7 to 1.0.

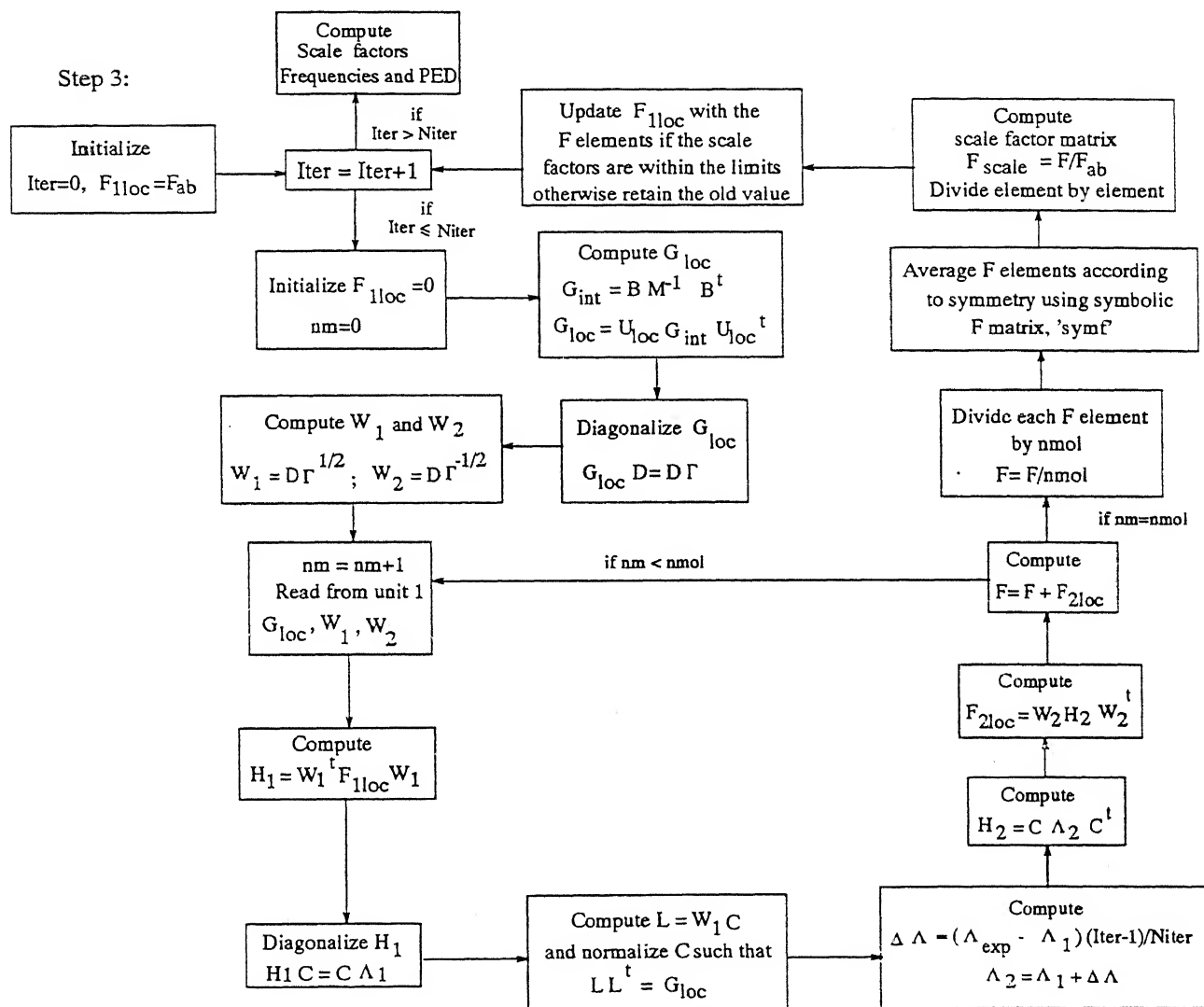


Figure 3.1: Flowchart of the fitting algorithm

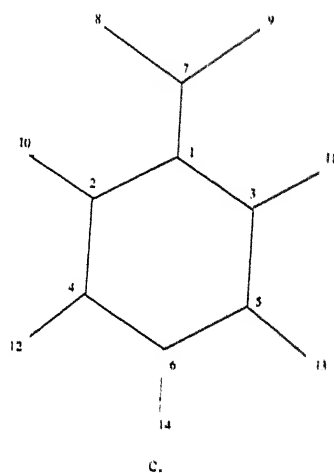
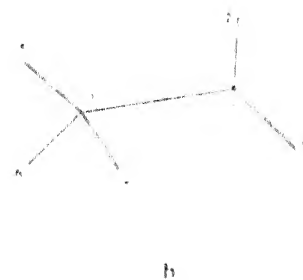
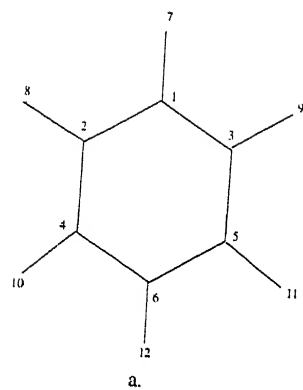


Figure 3.2: Atom numberings of a. benzene b. acetaldehyde c. benzaldehyde

Table 3.1: Force constants obtained after fitting to 'simulated frequencies' of different accuracies of four isotopomers of  $C_6H_6$

Symmetry blocks	F-matrix elements	Random scaling with factors between 1/0.6 and 1.0				Ozkabak-Goodman <sup>c</sup>
		A	B	C	D	
$A_{1g}$	$F_{1,1}$	7.631	7.599	7.615	7.616	7.616
	$F_{1,2}$	0.167	0.169	0.168	0.157	0.157
	$F_{2,2}$	5.559	5.553	5.556	5.554	5.554
$A_{2g}$	$F_{3,3}$	0.879	0.876	0.877	0.877	0.877
$B_{1u}$	$F_{12,12}$	0.659	0.656	0.657	0.658	0.658
	$F_{12,13}$	-0.234	-0.235	-0.234	-0.239	-0.237
	$F_{13,13}$	5.573	5.566	5.570	5.572	5.571
$B_{2u}$	$F_{14,14}$	3.944	3.934	3.939	3.939	3.939
	$F_{14,15}$	0.299	0.298	0.298	0.298	0.298
	$F_{15,15}$	0.830	0.826	0.828	0.828	0.828
$E_{1u}$	$F_{18,18}$	0.929	0.925	0.927	0.927	0.926
	$F_{18,19}$	0.211	0.208	0.209	0.209	0.209
	$F_{18,20}$	0.161	0.161	0.161	0.160	0.151
	$F_{19,19}$	7.387	7.364	7.376	7.381	7.380
	$F_{19,20}$	0.579	0.573	0.576	0.584	0.572
	$F_{20,20}$	5.571	5.563	5.567	5.568	5.568

A. Frequencies rounded to nearest integer +1.0

B. A-2.0 C. A-1.0 D. rounded to one decimal

e. Ref. 2.

Table 3.2: Calculated(4-21G) and Experimental frequencies<sup>a</sup> of acrolein and acrolein-d<sub>1</sub>

acrolein-h <sub>4</sub>				acrolein-d <sub>1</sub>			
This	SQM	Expt.	PED <sup>b</sup>	This	SQM	Expt.	
method				method			
In-Plane							
3102	3115	3102	$\nu\text{CH}_2$	3102	3115	3101	
2994	3082	(3000)	$\nu\text{CH}'' + \nu\text{CH}_2$	2994	3082	(2988)	
2994	3024	3000	$\nu\text{CH}'' + \nu\text{CH}_2$	2994	3024	2988	
2780	2768	2777	$\nu\text{CH}'$	2058	2049	2060	
1725	1732	1723	$\nu\text{CO}$	1707	1713	1709	
1624	1623	1625	$\nu\text{C}=\text{C} + \delta\text{CH}_2$	1622	1622	1621	
1423	1434	1422	$\delta\text{CH}_2 + \rho\text{CH}'$	1402	1419	1403	
1363	1383	1361	$\rho\text{CH}' + \delta\text{CH}_2$	1059	1057	1060	
1276	1266	1276	$\rho\text{CH}'' + \rho\text{CH}_2 + \nu\text{C}=\text{C}$	1276	1266	1275	
1160	1149	1159	$\nu\text{C}-\text{C} + \rho\text{CH}'' + \rho\text{CH}_2$	1152	1145	1153	
914	910	913	$\rho\text{CH}_2 + \nu\text{C}-\text{C}$	876	877	877	
564	559	564	$\delta\text{CCO} + \nu\text{C}-\text{C} + \delta\text{CCC}$	561	557	561	
323	314	324	$\delta\text{CCC} + \delta\text{CCO}$	314	306	313	
Out-of-Plane							
998	1003	993	$\omega\text{CH}_2 + \omega\text{CH}'' + t\text{CH}_2$	997	1003	993	
976	1002	(980)	$t\text{CH}_2 + \omega\text{CH}' + \omega\text{CH}_2$	970	975	959	
961	969	959	$\omega\text{CH}' + \omega\text{CH}_2$	848	869	846	
588	580	589	$\omega\text{CH}'' + t\text{CH}_2$	551	546	556	
158	(158)	158	$\tau\text{CC}$	151	(151)	151	

a. Frequencies are taken from ref 1. b. All coordinates are according to ref 1.

Table 3.3: Fitted ab initio harmonic force field of benzene in different basis sets in terms of symmetry coordinates<sup>a,b</sup>

Symm. blocks	F-elem ents	A	B	C	D <sup>c</sup>	E <sup>c</sup>	OG <sup>d</sup>	4-21G	
								this <sup>e</sup>	SQM <sup>f</sup>
A <sub>1g</sub>	F <sub>1,1</sub>	7.610	7.610	7.610	7.610	7.610	7.616	7.604	7.609
	F <sub>1,2</sub>	0.137	0.137	0.137	0.137	0.136	0.157	0.100	0.110
	F <sub>2,2</sub>	5.526	5.526	5.526	5.526	5.526	5.554	5.185	5.218
A <sub>2g</sub>	F <sub>3,3</sub>	0.877	0.877	0.877	0.877	0.877	0.877	0.864	0.855
B <sub>1u</sub>	F <sub>12,12</sub>	0.652	0.652	0.652	0.652	0.652	0.658	0.653	0.650
	F <sub>12,13</sub>	-0.160	-0.161	-0.162	-0.162	-0.164	-0.237	-0.156	-0.184
	F <sub>13,13</sub>	5.565	5.566	5.566	5.566	5.568	5.571	5.219	5.154
B <sub>2u</sub>	F <sub>14,14</sub>	3.936	3.936	3.936	3.936	3.936	3.939	3.952	3.917
	F <sub>14,15</sub>	0.297	0.297	0.297	0.297	0.297	0.298	0.308	0.290
	F <sub>15,15</sub>	0.828	0.828	0.828	0.828	0.828	0.828	0.817	0.811
E <sub>2g</sub>	F <sub>6,6</sub>	0.644	0.641	0.642	0.643	0.641	0.644	0.647	0.639
	F <sub>6,7</sub>	-0.137	-0.134	-0.136	-0.137	-0.136	-0.136	-0.144	-0.123
	F <sub>6,8</sub>	0.296	0.308	0.305	0.302	0.320	0.308	0.306	0.280
	F <sub>6,9</sub>	-0.153	-0.146	-0.160	-0.159	-0.189	-0.140	-0.107	-0.125
	F <sub>7,7</sub>	5.539	5.538	5.547	5.546	5.568	5.510	5.164	5.156
	f <sub>7,8</sub>	0.087	0.101	0.099	0.097	0.096	0.054	0.061	0.061
	F <sub>7,9</sub>	0.036	0.040	0.042	0.040	0.056	-0.066	0.025	0.028
	F <sub>8,8</sub>	6.615	6.636	6.626	6.621	6.648	6.690	6.622	6.700
	F <sub>8,9</sub>	-0.392	-0.386	-0.389	-0.389	-0.386	-0.398	-0.411	-0.421
E <sub>1u</sub>	F <sub>9,9</sub>	0.902	0.903	0.902	0.902	0.902	0.895	0.898	0.881
	F <sub>18,18</sub>	0.926	0.926	0.926	0.926	0.926	0.926	0.916	0.910
	F <sub>18,19</sub>	0.212	0.212	0.212	0.212	0.212	0.209	0.221	0.221
	F <sub>18,20</sub>	0.002	0.003	0.004	0.004	0.002	0.151	0.003	0.006
	F <sub>19,19</sub>	7.362	7.362	7.364	7.364	7.361	7.380	7.352	7.270
	F <sub>19,20</sub>	0.226	0.230	0.225	0.222	0.232	0.572	0.159	0.175
	F <sub>20,20</sub>	5.524	5.524	5.523	5.522	5.525	5.568	5.165	5.185
A <sub>2u</sub>	F <sub>11,11</sub>	0.250	0.250	0.250	0.250	0.250	0.249	0.249	0.241
B <sub>2g</sub>	F <sub>4,4</sub>	0.202	0.202	0.202	0.202	0.202	0.202	0.201	0.193
	F <sub>4,5</sub>	0.249	0.249	0.249	0.249	0.250	0.249	0.248	0.236
	F <sub>5,5</sub>	0.520	0.520	0.520	0.520	0.520	0.519	0.520	0.505
E <sub>1g</sub>	F <sub>10,10</sub>	0.337	0.337	0.337	0.337	0.337	0.337	0.337	0.330
E <sub>2u</sub>	F <sub>16,16</sub>	0.160	0.160	0.160	0.160	0.160	0.160	0.159	0.162
	F <sub>16,17</sub>	-0.168	-0.168	-0.168	-0.168	-0.168	-0.168	-0.166	-0.168
	F <sub>17,17</sub>	0.419	0.419	0.419	0.419	0.419	0.420	0.419	0.418
		g 0.6-1.0	0.7-1.1	0.7-1.2	0.7-1.2	0.6-1.55			

A. HF/4-21G; B. HF/6-31G\* C. HF/6-311G\*\* D. HF/6-311++G\*\* E. MP2/6-311G\*\*

a. Non-redundant symmetry coordinates are as defined in ref 2. b.Symmetry coordinates for ring deformation and CH rock and wagg are multiplied by the respective bond lenth.  
c. Ab initio force constants are taken from ref 2. d. Ref 2. e. Experimental frequencies and reference geometry of Pulay et al.(ref.22) is used for comparison f. Ref 22. g. Scale factors range used for each basis set.

Table 3.4: Fitted ab initio harmonic frequencies of benzene in different basis sets

Symmetry blocks	HF/ 4-21G	HF/ 6-31G*	HF/ 6-311G**	HF/ 6-311++G**	MP2/ 6-311G**	Ozkabak- Goodman <sup>a</sup>	expt <sup>a</sup>
A <sub>1g</sub>	3184.0	3184.1	3184.1	3184.1	3184.0	3191.0	3191.0
	993.8	993.8	993.8	993.8	993.8	994.4	994.4
A <sub>2g</sub>	1366.7	1366.7	1366.7	1366.7	1366.7	1367.0	1367.0
B <sub>1u</sub>	3176.1	3176.2	3176.2	3176.2	3176.4	3166.3	3174.0
	1010.7	1010.6	1010.6	1010.6	1010.6	1014.4	1010.0
B <sub>2u</sub>	1309.5	1309.5	1309.5	1309.5	1309.5	1309.4	1309.4
	1149.7	1149.7	1149.7	1149.7	1149.7	1149.7	1149.7
E <sub>2g</sub>	3169.3	3169.4	3170.3	3170.1	3172.5	3167.5	3174.0
	1609.7	1609.7	1609.5	1609.6	1609.1	1609.9	1607.0
	1179.8	1179.8	1179.7	1179.7	1179.3	1178.2	1177.8
	607.4	607.4	607.4	607.4	607.4	607.2	607.8
E <sub>1u</sub>	3177.2	3177.3	3177.2	3177.1	3177.4	3181.9	3181.0
	1494.9	1494.8	1494.9	1494.9	1494.8	1494.4	1494.0
	1039.2	1039.2	1039.3	1039.3	1039.2	1038.3	1038.3
A <sub>2u</sub>	674.9	674.9	674.9	674.9	674.9	674.0	674.0
B <sub>2g</sub>	990.7	990.7	990.7	990.7	990.7	990.0	990.0
	707.5	707.5	707.5	707.5	707.5	707.0	707.0
E <sub>1g</sub>	847.8	847.8	847.8	847.8	847.8	847.1	847.1
E <sub>2u</sub>	966.4	966.4	966.4	966.4	966.4	967.0	967.0
	397.7	397.7	397.7	397.7	397.7	398.0	398.0

a. Ref 2.

Table 3.5: Fitted ab initio harmonic frequencies of  $C_6D_6$ ,  $C^{13}_6H_6$  and  $C^{13}_6D_6$ 

Symmetry blocks	$C_6D_6$			$^{13}C_6H_6$			$^{13}C_6D_6$	
	calc	O.G. <sup>a</sup>	expt <sup>a</sup>	calc	O.G.	expt	calc	expt
$A_{1g}$	2361.8	2366.1	2362.0	3172.9	3179.8	3167.0	2344.0	2343.0
	947.7	948.6	947.0	958.0	958.8	957.4	917.3	918.0
$A_{2g}$	1063.1	1063.3	0.0	1355.6	1354.1	0.0	1048.3	0.0
$B_{1u}$	2342.5	2326.7	2344.0	3166.5	3157.6	0.0	2326.8	0.0
	969.4	976.5	970.0	973.8	977.1	0.0	936.5	0.0
$B_{2u}$	1286.0	1286.3	1286.3	1270.3	1269.6	1270.1	1236.1	1236.3
	828.1	827.9	827.9	1138.6	1138.8	1138.4	827.7	828.0
$E_{2g}$	2335.7	2340.7	2332.0	3159.9	3157.6	0.0	2320.2	0.0
	1561.3	1559.8	1564.0	1556.1	1556.0	0.0	1504.3	0.0
	865.5	863.5	867.0	1172.1	1170.8	0.0	862.0	0.0
	579.7	579.1	580.5	585.5	585.3	584.2	561.2	561.3
$E_{1u}$	2350.4	2346.7	2345.9	3166.8	3172.2	3180.0	2333.6	2325.0
	1340.2	1342.5	1341.0	1464.7	1464.0	1463.0	1299.4	1301.0
	813.9	813.9	814.3	1019.2	1018.1	1018.4	807.7	808.6
$A_{2u}$	495.5	494.9	496.2	672.9			492.8	
$B_{2g}$	828.4	827.8	829.0	982.8			804.4	
	598.6	598.1	599.0	685.1			592.1	
$E_{1g}$	659.4	658.9	660.0	840.9			650.6	
$E_{2u}$	787.5	788.0	787.0	955.5			771.3	
	345.2	345.5	345.0	386.4			338.6	

a. Ref 2.



Table 3.6: Predicted frequencies of pyridine<sup>a</sup> using 4-21G basis set

C <sub>5</sub> H <sub>5</sub> N				C <sub>5</sub> D <sub>5</sub> N			
expt.	calc.		SQM	expt.	calc.		SQM
	indiv. <sup>b</sup>	overall <sup>b</sup>			indiv.	overall	
3079	3093	3108	3093	2294	2295	2309	2305
3077	3085	3098	3102	2281	2284	2295	2292
3065	3073	3086	3078	2271	2274	2285	2280
3042	3066	3080	3065	2252	2262	2273	2267
3034	3062	3074	3071	2248	2261	2270	2262
1581	1584	1585	1585	1550	1547	1542	1544
1574	1580	1578	1582	1537	1545	1538	1546
1483	1476	1480	1475	1339	1335	1335	1330
1437	1435	1436	1436	1298	1300	1298	1290
1355	1339	1345	1353	1228	1245	1236	1231
1227	1256	1246	1240	1041	1027	1032	1036
1217	1205	1207	1214	1009	993	994	1005
1146	1151	1153	1156	963	968	969	954
1069	1057	1058	1073	888	882	888	885
1052	1057	1058	1053	835	837	843	840
1030	1028	1029	1025	824	819	822	822
991	1005	1005	980	824	819	821	819
654	652	655	654	624	623	625	627
603	596	596	604	581	575	574	583

a. all coordinates and experimental frequencies are taken from ref 6  
b. indiv.- refers to fitting one molecule C<sub>6</sub>H<sub>6</sub> or C<sub>6</sub>D<sub>6</sub>, overall- refers to fitting two isotopic molecules simultaneously.

Table 3.7: Predicted frequencies of benzaldehyde using 4-21G basis set

Expt. <sup>a</sup>	Calc.	% Error	Expt.	Calc.	% Error
3099	3088	0.3	–	1035	–
3081	3078	0.1	1026	1030	-0.5
3065	3068	0.4	1026	1028	-0.2
3043	3058	-0.5	1003	1003	0.0
3034	3045	-0.4	996	987	0.9
2806	2834	-1.0	918	939	-2.2
1728	1728	0.0	(852)	844	1.0
1614	1609	0.3	825	827	-0.2
1603	1595	0.5	740	738	0.2
(1492)	1495	-0.2	688	681	1.0
1460	1461	0.0	649	652	-0.4
1387	1388	-0.1	617	616	0.1
1314	1326	-0.9	450	443	1.5
1292	1309	-1.4	437	441	-0.9
1202	1197	0.4	(400)	399	0.2
1168	1171	-0.3	224	232	-3.5
(1158)	1161	-0.2	217	215	1.0
1074	1080	-0.6	(126)	122	2.9

a. experimental frequencies are taken from ref 35 and numbers within paranthesis are taken from liquid phase spectra

Table 3.8: Fitted force field of acrolein\*

In-Plane									
C-C st	4.355								
C=C st	0.335	8.740							
C=O st	0.697	-0.108	12.136						
CH <sup>r</sup> st	0.009	0.093	0.046						
CH <sup>f</sup> st	0.097	0.053	0.467	4.914					
CH <sup>r</sup> st	-0.012	0.062	0.010	0.004	4.267				
CH <sup>f</sup> st	-0.008	0.117	0.007	0.009	0.002	5.240			
CCC de	0.227	0.283	0.051	-0.003	0.015	0.044			
CCO de	0.174	0.092	0.274	-0.114	-0.023	0.047	4.970		
CH <sup>r</sup> ro	0.168	-0.166	-0.009	-0.122	-0.147	0.012	-0.042	1.132	
CH <sup>f</sup> ro	0.182	-0.009	-0.390	-0.116	0.026	0.010	-0.003	0.246	1.282
CH <sub>2</sub> de	-0.006	-0.186	-0.003	0.026	0.030	-0.003	0.015	0.036	-0.091
CH <sub>2</sub> ro	0.028	0.007	0.029	-0.006	-0.008	0.061	0.050	-0.022	0.068
Out-of-Plane				-0.014	-0.003	0.092	-0.128	-0.072	-0.022
C-C to	0.0251							0.016	0.031
CH <sup>r</sup> wa	-0.007	0.247						0.012	0.002
C-H <sup>f</sup> wa	-0.003	-0.021	0.419					0.013	-0.003
CH <sub>2</sub> wa	-0.003	0.024	-0.008	0.272				-0.022	0.440
CH <sub>2</sub> wa	0.011	0.003	0.022	0.001	0.122			0.016	0.011
									0.564

\*All coordinates are as given in ref 1.



Table 3.11: Internal coordinates of acetaldehyde

C=O	= $r_1$
C-C	= $r_2$
C-H <sub>ald</sub>	= $r_3$
$\theta_1$	= $2\alpha_1 - \alpha_2 - \alpha_2$
$\theta_2$	= $\alpha_2 - \alpha_2$
C-H <sub>wag</sub>	= $\gamma$
C-C <sub>tor</sub>	= $\tau$

Table 3.12: Scale factors of acetaldehyde taken for prediction

	$r_1$	$r_2$	$r_3$	$\theta_1$	$\theta_2$	$\gamma$	$\tau$
$r_1$	0.831						
$r_2$	1.000	0.883					
$r_3$	0.833	0.808	0.798				
$\theta_1$	0.977	1.000	0.836	0.872			
$\theta_2$	0.706	0.890	1.000	0.753	0.797		
$\gamma$						0.761	
$\tau$							0.771

$r, \theta$  etc. are internal coordinates as defined in Table-3.11

Table 3.13: Internal coordinates of benzaldehyde

$r_1 =$	1-3	$a_{15} - a_{20} =$	$\beta_{1-6} (\beta = 217-317)$
$r_2 =$	3-5	$a_{21} - a_{26} =$	$\alpha_{1-6} (\alpha = 213)$
$r_3 =$	5-6	$a_{27} =$	178
$r_4 =$	6-4	$a_{28} =$	179
$r_5 =$	4-2	$a_{29} =$	879
$r_6 =$	2-1	$a_{30} =$	$\gamma C_7$
$r_7 =$	1-7	$a_{31} =$	$\gamma H_{11}$
$r_8 =$	3-11	$a_{32} =$	$\gamma H_{13}$
$r_9 =$	5-13	$a_{33} =$	$\gamma H_{14}$
$r_{10} =$	6-14	$a_{34} =$	$\gamma H_{12}$
$r_{11} =$	4-12	$a_{35} =$	$\gamma H_{10}$
$r_{12} =$	2-10	$a_{36} =$	$\gamma H_9$
$r_{13} =$	7-8	$a_{37} - a_{42} =$	$\tau_{1-6}$
$r_{14} =$	7-9	$a_{43} =$	$\tau_7$

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Table 3.15: Non-redundant scaled 4-21G force constants of benzaldehyde\*

1	1	6.753
2	1	.624    2    6.773
3	1	-.459    2    .662    3    6.747
4	1	.435    2    -.449    3    .657    4    6.640
5	1	-.427    2    .456    3    -.449    4    .665    5    6.908
6	1	.612    2    -.425    3    .419    4    -.458    5    .621    6    6.694
7	1	.331    2    -.037    3    -.079    4    -.042    5    -.057    6    .421    7    4.607
8	1	-.019    2    -.020    3    -.003    4    .101    5    .105    6    -.004    7    -.001
	8	5.169
9	1	-.102    2    .048    3    -.034    4    -.013    5    .034    6    -.069    7    .820
	8	.009    9    11.930
10	1	.042    2    .013    3    -.009    4    -.001    5    .005    6    .008    7    .077
	8	.003    9    .394    10    4.433
11	1	-.007    2    -.017    3    -.017    4    .001    5    .080    6    .105    7    -.053
	8	.009    9    .027    10    .001    11    5.218
12	1	-.019    2    -.002    3    .099    4    .099    5    -.002    6    -.020    7    .002
	8	.010    9    .003    10    .001    11    .002    12    5.155
13	1	.119    2    .099    3    -.002    4    -.020    5    -.019    6    -.001    7    -.005
	8	.001    9    .009    10    .015    11    .001    12    .004    13    5.095
14	1	-.004    2    .101    3    .101    4    -.004    5    -.020    6    -.018    7    -.001
	8	.003    9    .009    10    .003    11    .001    12    .010    13    .010    14    5.168
15	1	.464    2    .056    3    -.052    4    .098    5    -.054    6    -.624    7    -.270
	8	-.016    9    .040    10    -.105    11    .151    13    -.066    14    .016    15    5.511
16	1	-.413    2    .414    3    .036    4    -.040    5    .049    6    -.024    7    .034
	9	.034    10    -.033    11    -.014    12    .015    14    -.019    15    .004    16    3.608
17	1	-.029    2    -.439    3    .432    4    .027    5    -.048    6    .052    7    -.018
	8	.015    9    -.023    10    -.003    12    -.019    13    .022    15    -.101    16    .059
	17	3.583
18	1	.054    2    -.039    3    -.423    4    .416    5    .040    6    -.050    7    .005
	8	-.018    9    -.006    10    .002    11    .012    13    -.016    14    .019    15    -.020
	16	-.086    17    .056    18    3.589
19	1	-.052    2    .050    3    -.026    4    -.430    5    .432    6    .023    7    .011
	9	.013    10    .009    11    -.020    12    .019    14    -.015    15    -.073    16    -.007
	17	-.085    18    .057    19    3.576
20	1	.023    2    -.054    3    .049    4    -.025    5    -.401    6    .419    7    -.044
	8	.020    9    .083    10    -.009    12    -.014    13    .019    15    .065    16    -.092
	17	-.004    18    -.082    19    .054    20    3.499
21	7	-.458    8    -.161    9    -.048    10    -.038    11    .166    12    .163    13    .171
	14	-.162    21    4.505
22	1	.231    2    -.619    3    .338    4    .305    5    -.601    6    .180    7    -.497
	8	.080    9    -.087    10    -.044    11    .099    12    -.160    13    .087    14    .081
	16	-.288    17    .296    19    -.290    20    .328    22    4.390

Table 3.15 (Continued): Non-redundant scaled 4-21G force constants of benzaldehyde

23	1	.569	3	-.508	4	.503	6	-.541	7	.034	8	-.126	9	.016
	10	-.009	11	.129	13	-.144	14	.136	15	.321	16	-.170	17	-.171
	18	.350	19	-.170	20	-.156	23	4.240						
24	1	.143	2	.051	3	-.085	4	.021	5	-.008	6	-.077	7	.59
	8	-.002	9	.453	10	-.263	11	-.090	12	.006	13	.010	14	.01
	15	.381	16	-.021	17	-.032	18	.011	19	-.026	20	-.041	21	-.05
	22	-.165	23	.227	24	3.645								
25	1	-.015	2	.003	3	-.007	4	-.012	5	.008	6	.078	7	.40
	8	.005	9	-.528	10	.071	11	.003	12	.000	13	.022	14	.00
	15	-.289	16	-.025	17	-.001	18	.003	19	.021	20	.003	21	-.09
	22	-.088	23	-.046	24	.204	25	2.207						
26	26	1.198												
27	26	.045	27	1.160										
28	26	-.072	27	.042	28	1.117								
29	26	-.118	27	-.081	28	.051	29	1.183						
30	26	-.088	27	-.103	28	-.076	29	.051	30	1.127				
31	26	.020	27	-.076	28	-.103	29	-.079	30	.049	31	1.221		
32	26	-.142	27	-.030	28	.022	29	.016	30	-.001	31	-.060	32	1.633
33	26	.098	27	-.110	28	.089	29	-.101	30	.096	31	-.085	32	.086
	33	1.305												
34	27	-.098	28	.004	30	-.085	31	.016	32	.083	34	1.059		
35	26	.045	27	.062	28	-.111	29	.049	30	.056	31	-.092	32	.020
	35	1.086												
36	26	-.066	27	-.018	28	.031	29	.010	30	-.019	31	-.013	32	.063
	33	.007	34	.042	35	-.082	36	.418						

\* Non-redundant local coordinates are according to Table-3.14.



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## Chapter 4

# Force Field and Assignment of the Vibrational Spectra of Naphthalene and Anthracene

The vibrational spectra of polyaromatic hydrocarbons and their cations received much attention recently due to their importance as the origin of infrared emission bands in the interstellar radiation from many galactic sources [1]. Naphthalene is the smallest member in the family and was studied by several authors [2-18]. Pulay et al. reported for the first time a complete theoretical force field of naphthalene obtained by using the scale factors from their benzene work [3]. However benzene and naphthalene are not really structurally related (naphthalene is a coupled ring system) and the direct transfer of scale factors from benzene leads to poor predicted numbers. A geometry refinement which includes the approximate cubic force constants was needed to obtain a good fit between experimental and predicted frequencies of naphthalene. Also, the number of force constants listed for naphthalene (208) is more than the number of symmetric force constants (189). More recently the vibrational spectra of naphthalene and its radical cation were studied using matrix isolation spectroscopy by Szczepanski et al. [2]. The second simplest member, anthracene, is also studied by several theoretical and experimental methods [19-28]. The early work of Bruhn and Mecke [21] and Califano [22] identified many of the fundamental frequencies of anthracene and anthracene- $d_{10}$  based on their polarization measurements. The IR spectra of anthracene and anthracene- $d_{10}$  crystals were analyzed by Bree and Kydd [23]. Bekke et al. using a five parameter approximation analyzed all the in-plane fun-

damentals of anthracene and proposed their probable assignments [20]. More recently, Szczepanski et al. analyzed the vibrational spectra of anthracene and its radical cation using matrix isolation spectroscopy [19]. On the theoretical side, a detailed calculation of the normal modes of anthracene and anthracene- $d_{10}$  was reported by Krainov using the complete system of induction coefficients from naphthalene [25]. A simplified valence force field calculation for benzene, naphthalene and anthracene was reported by Neto et al. [9]. Evans and Scully [26] reported a theoretical calculation for the out of plane vibrations of anthracene, anthracene- $d_2$  and anthracene- $d_{10}$  by transferring the benzene force constants. Although a number of vibrational spectral studies have been reported for anthracene, some of the assignments still remain uncertain and the complete force field is not yet available. In this chapter we report the ab initio force field of naphthalene and anthracene at the HF/4-21G level. We explicitly show that the benzene molecule is not structurally related to anthracene whereas naphthalene and anthracene are structurally related. Using the newly developed methodology described in chapter 3 we report a set of 189 non-redundant local force constants which reproduces the naphthalene fundamental frequencies with an average error of  $5.7 \text{ cm}^{-1}$ . The scale factors obtained from naphthalene force constants were used to obtain the complete anthracene force field which simulates the vibrational spectra of anthracene with remarkable accuracy. It is to be noted that *no experimental data* is used in the *prediction* of anthracene frequencies.

## 4.1 Calculations

The ab initio force constants and frequencies of naphthalene and anthracene were calculated using 4-21G basis set. The cartesian force constant matrices were then transformed to the non-redundant local coordinate space. The non-redundant local coordinates of naphthalene and anthracene are shown in Table-4.1 and Table-4.2 and in Figure 4.1 and Figure 4.2. The number of force constants getting adjusted due to the change in frequencies is smaller when the fitting is done in symmetry blocks compared to local coordinates. Also mixing between degenerate modes is avoided by fitting the frequencies in symmetry

coordinates. Hence the fitting is done in symmetry coordinates adjusting the scale factors in local coordinates. A flow chart of the modified algorithm is given in Figure 4.3.

## 4.2 Results

As pointed out by Pulay et al. [3] in their SQM study of naphthalene, the naphthalene force field is quite different from that of benzene and hence simple transfer of benzene force field would poorly reproduce the naphthalene fundamental vibrational frequencies. So, our present method also fails to achieve a better fit for naphthalene by simple transfer of benzene scale factors largely because of the absence of inter-ring C-C-C couplings in benzene. However, it is possible to predict the vibrational frequencies of anthracene from naphthalene as naphthalene and anthracene resemble each other even in C-C-C couplings. Because the prediction requires a complete set of scale factors, we fitted the experimental frequencies of naphthalene- $d_0$  and - $d_8$  to the theoretically calculated ab initio HF/4-21G force field. The fitting produced an excellent agreement between the experimental and the calculated frequencies. The average deviation is  $5.7\text{cm}^{-1}$  ( $4.0\text{cm}^{-1}$  in  $\text{C}_{10}\text{D}_8$ ) including C-H frequencies and  $3.6\text{cm}^{-1}$  ( $2.4\text{cm}^{-1}$  in  $\text{C}_{10}\text{D}_8$ ) excluding C-H frequencies.

### 4.2.1 Force Field of Naphthalene and Anthracene

The force constant values obtained for benzene are 6.715 for C-C stretch, 5.181 for C-H stretch, 0.510 for C-H deformation, 1.274 and 1.239 for ring deformation and 0.319 and 0.388, 0.307 are for out of plane C-H wag and ring bending respectively. These when compared to naphthalene force constants indicate clearly that the benzene force field is very different from that of naphthalene. For naphthalene our fitted force field shows a good agreement with the earlier SQM predicted force field in both in-plane and out of plane diagonal force constants. Obviously such a good agreement is not expected in the case of the coupling constants because of the oversimplification involved in the evaluation of the coupling force constants in the SQM procedure. The fitted force field produced frequencies for both naphthalene and naphthalene- $d_8$  better than the earlier SQM prediction so

can be considered as an improvement over the earlier force field. A representative set of force constants of naphthalene and anthracene is listed in Table-4.3 and the complete force field is given in Tables-4.9 to 4.12 from which we can draw the following conclusions.

(1) C-H diagonal force constants of naphthalene and anthracene are almost identical except for a minor deviation of the anthracene central ring. Interactions involving C-H bonds( $\sigma$  bond) are small and only the first neighbours contribute significantly.

(2) C-C force constants exhibit similar trends although the absolute values are different because of  $\pi$ - $\pi$  interaction. The trend and the accuracy of the predicted C-C frequencies indicate the transferability of the scale factors. The diagonal force constants are in accordance with the Huckel  $\pi$  bond order [29]. Interactions involving C-C bonds( $\sigma$  and  $\pi$  bonds) are much stronger and extend over the entire ring in both systems confirming the earlier preliminary conclusion based on only naphthalene [30].

(3) Diagonal  $f_{\beta_i}$ s are almost the same for the naphthalene and anthracene.  $\text{CH}_i - \beta_i$  interactions are less than 0.01 and negligible in most cases.  $\text{CC}_i - \beta_i$  interactions are substantial only for the connecting bonds. For outer rings of naphthalene and anthracene they are almost the same while central ring has slightly higher values.

(4) Diagonal ring deformation force constants are similar for naphthalene and the outer rings of anthracene and somewhat higher for the central ring.

These conclusions clearly indicate that the force field of the outer rings of anthracene is almost identical with that of naphthalene and the central ring differ to some extent. As a result the prediction is excellent for the outer ring modes of anthracene and the deviation is slightly more from the experimental frequencies for the central ring.

### 4.2.2 Vibrational Spectra of Naphthalene

The 48 normal modes of naphthalene in  $D_{2h}$  symmetry factorize in 8 symmetry blocks as  $9A_g, 8B_{3g}, 8B_{1u}, 8B_{2u}, 4A_u, 4B_{3u}, 3B_{1g}$  and  $4B_{2g}$ . The calculated fundamentals from the fitting procedure of naphthalene -d<sub>0</sub> and -d<sub>8</sub> are given in Table-4.4 along with their assignments. The assignments agree well with that of Pulay et al. in almost all the modes. However there is a controversy regarding one of the  $B_{2u}$  fundamentals. It could be at 1144 or 1163

$\text{cm}^{-1}$ . In the SQM method, the predicted number  $1158 \text{ cm}^{-1}$  was closer to  $1163 \text{ cm}^{-1}$ . We tried fitting both the frequencies separately.  $1163 \text{ cm}^{-1}$  gave the C-C force constant in agreement with the expected bond orders. As a result we assigned it at  $1163 \text{ cm}^{-1}$ . In  $\beta_{1u}$ , the band at  $810 [9,11-12]$  and  $748 \text{ cm}^{-1} [6]$  were suggested as possible alternatives for the  $\delta_1 + \delta_3$  mode. The fitting using  $810 \text{ cm}^{-1}$  produced  $805 \text{ cm}^{-1}$  as the calculated fundamental while the  $748 \text{ cm}^{-1}$  produced  $765 \text{ cm}^{-1}$  as the calculated frequency. This clearly indicates that  $810 \text{ cm}^{-1}$  band is more likely to be the correct one and this is in agreement with the earlier SQM assignment.

### C-H stretching vibrations:

Due to anharmonicity and the perturbations because of Fermi resonance the C-H fundamentals are *difficult to assign*. However, we used the following strategy to address the effect of anharmonicity on the naphthalene frequencies. We started with the assumption that the anharmonicity of the C-H and C-D bonds are the same for benzene and naphthalene because the C-H force constants are nearly same ( $5.181\text{-C}_6\text{H}_6$ ,  $5.113\text{-}\alpha\text{-C}_{10}\text{H}_8$  and  $5.153\text{-}\beta\text{-C}_{10}\text{H}_8$ ) and the C-H and C-D stretching frequencies appear in the same narrow range of frequencies. The harmonic frequencies could be estimated from the equation

$$\omega_i = \nu_i + \Delta_i \quad (1)$$

where  $\Delta_i$  represents the total anharmonic corrections to the fundamental frequency. Following Goodman et al. [31] we adopted a  $117 \text{ cm}^{-1}$  anharmonic correction for C-H fundamentals and  $59 \text{ cm}^{-1}$  for C-D ones. The second assumption we made is that the deuterated fundamentals are not perturbed by Fermi resonance because there is no frequency in the  $1100\text{-}1150 \text{ cm}^{-1}$  range whose overtone can interact with the C-D fundamentals ( $2200\text{-}2400 \text{ cm}^{-1}$ ). (However, it is possible to have a combination band of the right frequency. We neglect such a possibility because without further experimental data this problem could not be addressed). The best fitted C-D fundamentals are converted to harmonic frequencies based on equation (2) and fitted to get the harmonic force constants. During the fitting all  $\text{C}_{10}\text{H}_8$  and  $\text{C}_{10}\text{D}_8$  frequencies other than C-H stretching ones are used. The computed harmonic force constants are in good agreement with the benzene value obtained by Goodman et al. [31] ( $5.367\text{-C}_6\text{H}_6$ ,  $5.459\text{-}\alpha\text{-C}_{10}\text{H}_8$  and  $5.486\text{-}\beta\text{-C}_{10}\text{H}_8$ ). These harmonic



force constants are used to predict the harmonic C-H frequencies which in turn used to calculate the corresponding anharmonic frequencies using equation 4.1. The predicted anharmonic frequencies agree well with the observed fundamentals except for one of the  $B_{3g}$  modes ( $3031\text{ cm}^{-1}$ ) as shown in Table-4.5 indicating that this particular frequency is a likely candidate for Fermi resonance. The computed mean amplitudes of vibration (Figure 4.4) are in good agreement with the reported values [32,33] indicating that the final force field is reliable.

### 4.2.3 Vibrational Spectra of Anthracene

Anthracene is planar with  $D_{2h}$  symmetry and is characterized by 66 vibrational degrees of freedom. The 45 in-plane and 21 out of plane normal vibrations span the irreducible representations as  $12A_g + 11B_{3g} + 11B_{1u} + 11B_{2u} + 4b_{1g} + 6b_{2g} + 5a_{1u} + 6b_{3u}$ . The fundamental frequencies of anthracene are predicted separately by transferring scale factors of benzene and naphthalene respectively. Table-4.6 shows the predicted frequencies obtained from the scale factors of benzene and naphthalene along with their assignments. The table clearly indicates that transferring the diagonal force constants and taking their geometric mean for the off-diagonal elements give poor agreement compared to transferring all the scale factors. When the molecules are structurally related the assumption that each force constant is associated with its own scale factor, works well rather than the geometric mean of diagonal force constants for the off-diagonal elements because the characteristics of each force constant is retained. The average deviations for the 66 frequencies are 15.0, 13.5 and  $9.2\text{ cm}^{-1}$  (13.6, 13.2 and  $8.2\text{ cm}^{-1}$  excluding CH stretch) for the different predictions as shown in Table-4.6. As expected the predicted anthracene frequencies from naphthalene scale factors are better than those predicted from benzene even in geometric mean approximation. In the prediction, corrections for basis set error, correlation and anharmonicity were transferred through scale factors from naphthalene to anthracene.

#### 4.2.4 In-plane frequencies

##### C-H stretching vibrations:

The  $\nu$ C-H frequencies appear as independent modes and all the C-H stretching fundamentals appear in the region  $\nu > 3000 \text{ cm}^{-1}$ . To address the problem of anharmonicity, the harmonic scale factors are transferred from naphthalene to anthracene to predict the harmonic frequencies. The harmonic frequencies are then corrected for anharmonicity as in the case of naphthalene. The final values are given in Table-4.5 along with the experimental numbers. The agreement is good for six frequencies indicating the other four are possibly perturbed by Fermi resonance.

##### $A_g$ modes:

The frequencies in this block is only Raman active, and the earlier assignments proposed by several authors are quite consistent and agree within the experimental error. One of the  $R_{CC}$  band in the earlier assignment was doubtful, either at  $1412$  or  $1400 \text{ cm}^{-1}$  [20], which was resolved later assigning  $1412 \text{ cm}^{-1}$  to  $A_{1g}$  mode and  $1400 \text{ cm}^{-1}$  to  $B_{2u}$  fundamental [19]. The predicted numbers  $1408 \text{ cm}^{-1}$  and  $1404 \text{ cm}^{-1}$  agree very well with the later assignment. The prediction is poor only in the case of  $1264 \text{ cm}^{-1}$  band with a deviation of  $21 \text{ cm}^{-1}$ . This is clearly due to the differences between the naphthalene and anthracene force constants for the diagonal  $R_1, R_7$  and their interactions.

##### $B_{3g}$ modes:

In this block a weak Raman band observed by Bakke et al. [20] at  $1574 \text{ cm}^{-1}$  was assigned at  $1596 \text{ cm}^{-1}$  by Neto et al. [9] and Colombo [24]. Our predicted number  $1596 \text{ cm}^{-1}$  exactly matches with the latter assignment. So we confirm this mode at  $1596 \text{ cm}^{-1}$ . With this modification all predicted frequencies match well with the earlier assignments except the one at  $1433 \text{ cm}^{-1}$ . This band shows a deviation of  $55 \text{ cm}^{-1}$ , the predicted one being at  $1388 \text{ cm}^{-1}$ . It is unlikely that the force fields of naphthalene and anthracene are very different to cause this much error. It is likely that either this assignment is incorrect or something like Fermi interaction occurs for this mode. Bakke et al. observed a Raman band at  $1384 \text{ cm}^{-1}$  [20] which agrees well the predicted value of  $1388 \text{ cm}^{-1}$ . It is interesting to note that the earlier calculated values based on NCA also occur at  $1389 \text{ cm}^{-1}$  [9] and  $1396 \text{ cm}^{-1}$  [25].

**B<sub>1u</sub> modes:**

These IR and Raman active bands are available from the more recent work [19]. The agreement with the earlier experimental numbers are within few  $\text{cm}^{-1}$ , except for the one at  $1346 \text{ cm}^{-1}$ . The earlier workers assigned this band at around  $1317 \text{ cm}^{-1}$  [9,20-24,28]. The predicted frequency at  $1340 \text{ cm}^{-1}$  agrees well with the recent assignment. All the other predicted numbers in this block agree very well with the experimental numbers.

**B<sub>2u</sub> modes:**

This is probably the most controversial block in the anthracene spectra. Deviations of  $100\text{-}150 \text{ cm}^{-1}$  could be found in the existing assignments. The  $R_{CC}$  band is assigned at different frequencies by different authors.  $1695$  [23],  $1720$  [24],  $1690$  [20],  $1533$  [9,22] and  $1524$  [28]  $\text{cm}^{-1}$  are some of the available assignments. The most recent work [19] assigned it at  $1542 \text{ cm}^{-1}$ . The predicted number  $1560 \text{ cm}^{-1}$  confirms this assignment. The other controversial bands were assigned at  $1460, 1400$ , and  $1318 \text{ cm}^{-1}$  in the latest work [19]. For the  $1460 \text{ cm}^{-1}$  fundamental earlier assignments were made at  $1534$  [20],  $1533$  [23],  $1680$  [24] and  $1462$  [9,22]. The predicted number appear at  $1445 \text{ cm}^{-1}$  is in agreement with  $1460 \text{ cm}^{-1}$ . The  $1400 \text{ cm}^{-1}$  band was assigned at  $1494$  [20],  $1398$  [9,22],  $1495$  [23],  $1537$  [24] and  $1350$  [28]  $\text{cm}^{-1}$ . Our predicted frequency  $1404 \text{ cm}^{-1}$  confirms the assignment at  $1400 \text{ cm}^{-1}$ . The predicted frequency corresponding to the experimental  $1318 \text{ cm}^{-1}$  band [19] occurs at  $1283 \text{ cm}^{-1}$ , off by  $33 \text{ cm}^{-1}$ . This band corresponds to  $(R_7 + \beta_5)$  which represent the central ring and there is no exact counterpart of this in naphthalene. Hence, the deviation is higher than the expected one.

## 4.2.5 Out of plane frequencies

**A<sub>1u</sub> modes:**

This class is inactive in both Raman and IR spectra of the free molecule and hence comparison is made with the IR active crystal bands. Only three out of five fundamentals were reported [20,21,27]. The highest frequency mode was assigned at  $988 \text{ cm}^{-1}$  [20] and  $979 \text{ cm}^{-1}$  [27]. The predicted value  $984 \text{ cm}^{-1}$  is closer to the first one. The other two bands agree between the different authors as well as with the predicted ones. For the two lower

frequencies the predictions are at 491 and 126  $\text{cm}^{-1}$ . Early work of Chantry et al. [27] gives the experimental frequency at 126  $\text{cm}^{-1}$ .

#### **$B_{3u}$ modes:**

The highest frequency in this symmetry is assigned at around 956 [2,20-24,27] and at 920  $\text{cm}^{-1}$  [28]. The predicted frequency 970  $\text{cm}^{-1}$  supports the higher number in agreement with most of the literature. The next higher band is assigned at 883  $\text{cm}^{-1}$  [20] and 879  $\text{cm}^{-1}$  [19]. These are within experimental error and we took the most recent value of 879  $\text{cm}^{-1}$  for the predicted value 895  $\text{cm}^{-1}$ . The other three numbers are in excellent agreement with the most recent paper [19]. It is of interest to note that the torsional numbers  $> 300 \text{ cm}^{-1}$  were predicted very well compared to the out of plane wag fundamentals. Again this is a reflection of the differences in force fields between naphthalene and anthracene. It is known that the ab initio method gives very low value for the torsions below 300  $\text{cm}^{-1}$ .

#### **$B_{1g}$ and $B_{2g}$ modes:**

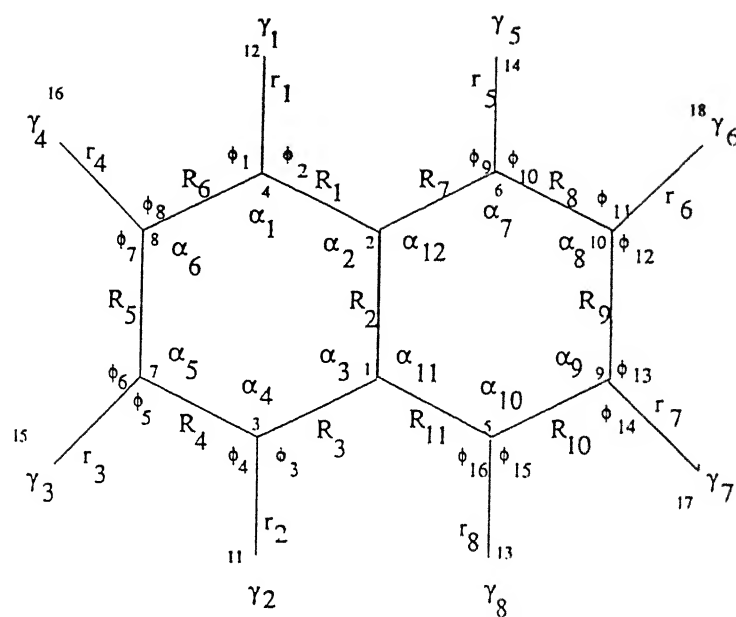
The earlier work of Evans and Scully [26] do not agree with that of bakke et al. [20]. It appears that the only reliable values are that of Bakke et al. [20] for these modes. Although there is overall agreement between the predicted and the experimental frequencies, deviations are quite large in three of the fundamentals assigned at 896,773 and 580  $\text{cm}^{-1}$ . The 896  $\text{cm}^{-1}$  band if assigned at 852  $\text{cm}^{-1}$  [26] gives better agreement with the predicted 831  $\text{cm}^{-1}$ . An experimental reinvestigation of these frequencies may give a better agreement with the prediction.

The symbolic force constant matrices in terms of symmetry unique local force constants and the orthogonal transformation matrices from local to symmetric coordinates for naphthalene and anthracene and the complete mean amplitudes of vibration of naphthalene are given in Tables-4.7 to 4.13.

## **4.3 Conclusions**

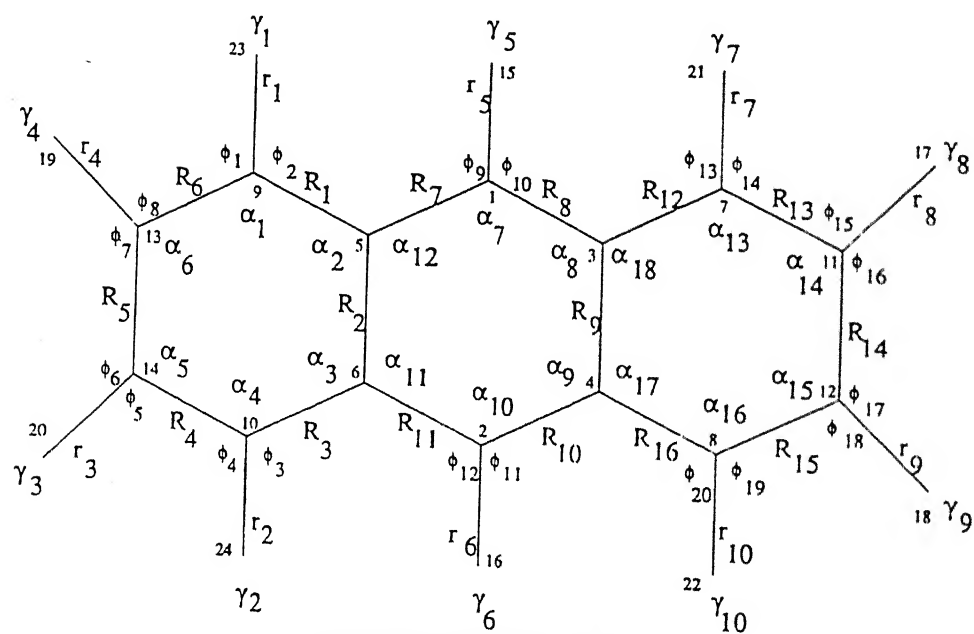
The fitting procedure to obtain the scale factors and frequencies from the ab initio force field has shown to be remarkably successful for naphthalene producing an average devi-

ation of  $5.7\text{ cm}^{-1}$  between the predicted and experimental frequencies. These scale factors when used to predict the frequencies of anthracene, the results are in excellent agreement with the experimental ones with an average average deviation of  $8.2\text{ cm}^{-1}$  for a molecule of 24 atoms. From the accuracies of the computed frequencies it is clear that the methodology could be used successfully for the prediction of frequencies of unknown molecules. The earlier assignments of naphthalene were confirmed and the anthracene assignments were either confirmed or reassigned. A complete set of non-redundant force constants are obtained for both naphthalene and anthracene.



$\tau$  numberings are same as defined in R

Figure 4.1: Internal coordinates of naphthalene



$\tau$  numberings are same as defined in R

Figure 4.2: Internal coordinates of anthracene

Step 1: Convert cartesian force constants obtained from the ab initio program to force constants in local symmetry coordinates as recommended by Pulay et al. We refer to this F matrix as  $F_{ab}$

Step 2: Input: No. of isotopic species(nmol), masses(M), Wilson's B matrix(B), local U ( $U_{loc}$ ), orthogonal U ( $U_{ortho}$ ) - transformation matrix from local U to symmetric U. We used Niter=1000.

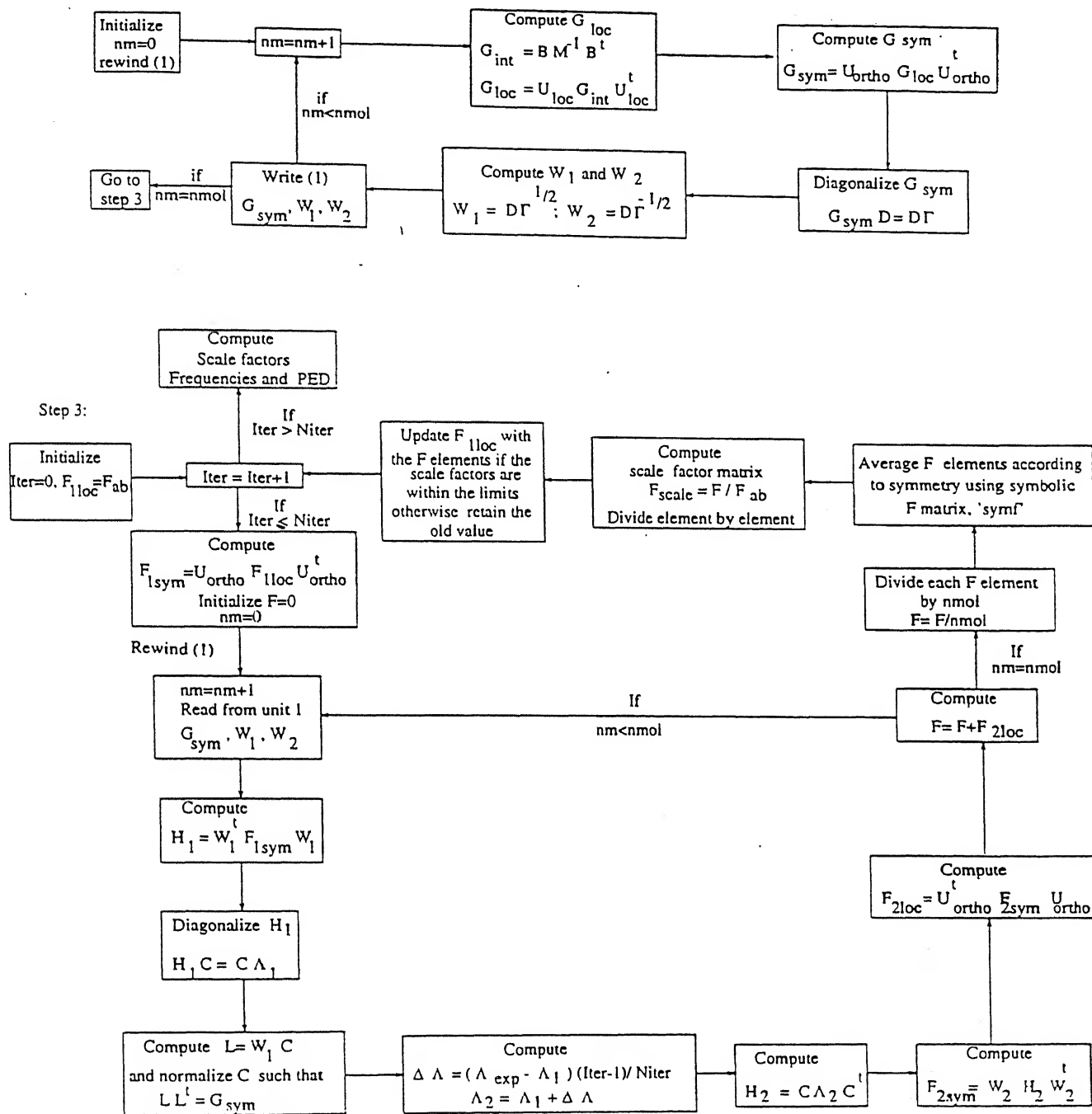


Figure 4.3: Flowchart of the modified algorithm

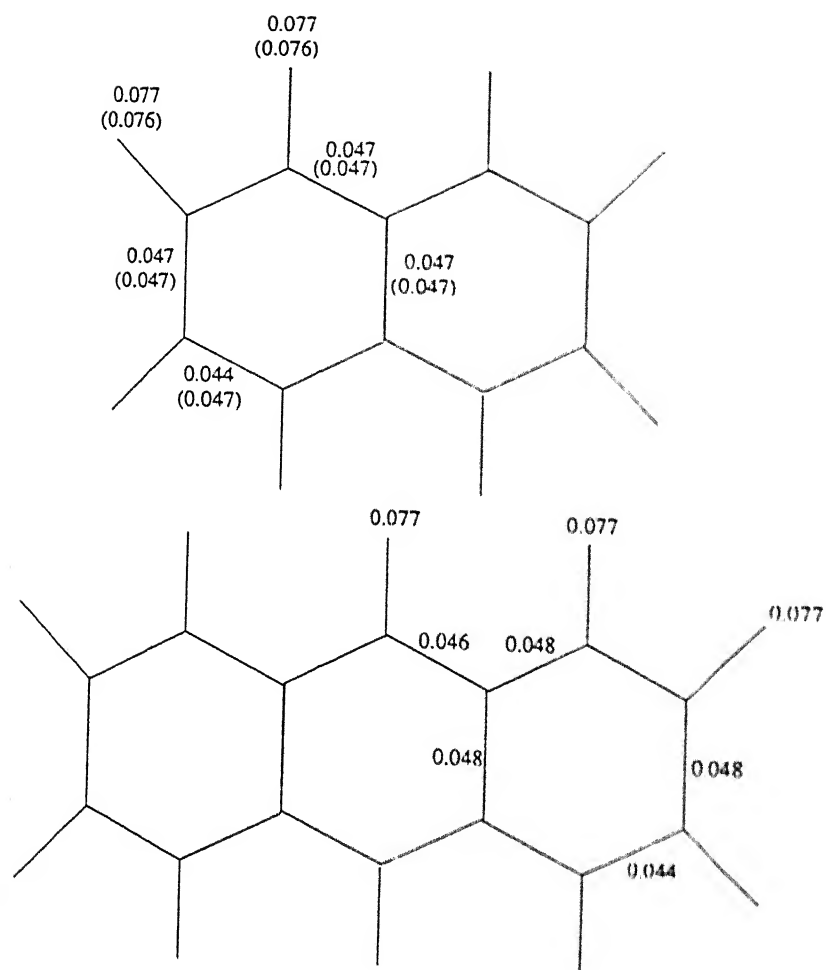


Figure 4.4: Mean amplitudes of vibration of naphthalene and anthracene (Å)

Numbers are obtained from our predicted force field. Numbers in the parentheses are observed values taken from ref. 33.



Table 4.1: Non-redundant local coordinates of naphthalene

In plane	
$S_{1-11}$	$= R(\text{CC-stretch})(R_i)$
$S_{12-19}$	$= r(\text{CH-stretch})(r_i)$
$S_{20-27}$	$= 2^{-1/2}(\phi_1-\phi_2); 2^{-1/2}(\phi_3-\phi_4); \dots$ etc. (CH-deform.)( $\beta_i$ )
$S_{28,31}$	$= 6^{-1/2}(\alpha_1-\alpha_2+\alpha_3-\alpha_4+\alpha_5-\alpha_6)$ (ring deform.)( $\delta_1, \delta_4$ )
$S_{29,32}$	$= 12^{-1/2}(2\alpha_1-\alpha_2-\alpha_3+2\alpha_4-\alpha_5-\alpha_6)$ (ring deform.)( $\delta_2, \delta_5$ )
$S_{30,33}$	$= 2^{-1/2}(\alpha_2-\alpha_3+\alpha_5-\alpha_6)$ (ring deform.)( $\delta_3, \delta_6$ )
Out of plane	
$S_{1-8}$	$= \gamma(\text{CH-wagg})(\gamma_i)$
$S_{9,12}$	$= 6^{-1/2}(\tau_1-\tau_2+\tau_3-\tau_4+\tau_5-\tau_6)$ (ring torsion)( $\tau_1, \tau_4$ )
$S_{10,13}$	$= 12^{-1/2}(\tau_1-2\tau_2+\tau_3+\tau_4-2\tau_5+\tau_6)$ (ring torsion)( $\tau_2, \tau_5$ )
$S_{11,14}$	$= 2^{-1/2}(\tau_1-\tau_3+\tau_4-\tau_6)$ (ring torsion)( $\tau_3, \tau_6$ )
$S_{15}$	$= \tau_{3126}-\tau_{4215}(\tau)$

\*All internal coordinates are according to figure-4.1.

Table 4.2: Non-redundant local coordinates\* of anthracene

In plane	
$S_{1-16}$	$= R(\text{CC-stretch})(R_i)$
$S_{17-26}$	$= r(\text{CH-stretch})(r_i)$
$S_{27-36}$	$= 2^{-1/2}(\phi_1-\phi_2); 2^{-1/2}(\phi_3-\phi_4); \dots$ etc. (CH-deform.)( $\beta_i$ )
$S_{37,40,43}$	$= 6^{-1/2}(\alpha_1-\alpha_2+\alpha_3-\alpha_4+\alpha_5-\alpha_6)$ (ring deform.)( $\delta_1, \delta_4, \delta_7$ )
$S_{38,41,44}$	$= 12^{-1/2}(2\alpha_1-\alpha_2-\alpha_3+2\alpha_4-\alpha_5-\alpha_6)$ (ring deform.)( $\delta_2, \delta_5, \delta_8$ )
$S_{39,42,45}$	$= 2^{-1/2}(\alpha_2-\alpha_3+\alpha_5-\alpha_6)$ (ring deform.)( $\delta_3, \delta_6, \delta_9$ )
Out of plane	
$S_{1-10}$	$= \gamma(\text{CH-wagg})(\gamma_i)$
$S_{11,14,17}$	$= 6^{-1/2}(\tau_1-\tau_2+\tau_3-\tau_4+\tau_5-\tau_6)$ (ring torsion)( $\tau_1, \tau_4, \tau_7$ )
$S_{12,15,18}$	$= 12^{-1/2}(\tau_1-2\tau_2+\tau_3+\tau_4-2\tau_5+\tau_6)$ (ring torsion)( $\tau_2, \tau_5, \tau_8$ )
$S_{13,16,19}$	$= 2^{-1/2}(\tau_1-\tau_3+\tau_4-\tau_6)$ (ring torsion)( $\tau_3, \tau_6, \tau_9$ )
$S_{20}$	$= \tau_{7342}-\tau_{1348}(\tau')$
$S_{21}$	$= \tau_{15610}-\tau_{9562}(\tau'')$

\*All internal coordinates are according to figure-4.2.

Table 4.3: Selected scaled force constants of naphthalene and anthracene\*

Naphthalene			Anthracene		
local coordinates	force constants	$\pi$ bond order	local coordinates	force constants	$\pi$ bond order
(R <sub>1</sub> ,R <sub>3</sub> ,R <sub>7</sub> ,R <sub>11</sub> )	6.076	0.554	(R <sub>1</sub> ,R <sub>3</sub> ,R <sub>12</sub> ,R <sub>16</sub> )	5.695	0.554
(R <sub>4</sub> ,R <sub>6</sub> ,R <sub>8</sub> ,R <sub>10</sub> )	7.513	0.725	(R <sub>4</sub> ,R <sub>6</sub> ,R <sub>13</sub> ,R <sub>15</sub> )	7.988	0.725
(R <sub>5</sub> ,R <sub>9</sub> )	6.112	0.603	(R <sub>5</sub> ,R <sub>14</sub> )	5.703	0.586
(R <sub>2</sub> )	5.607	0.518	(R <sub>2</sub> ,R <sub>9</sub> )	5.242	0.486
(R <sub>1</sub> ,r <sub>1</sub> )	0.060		(R <sub>1</sub> ,r <sub>1</sub> )	0.057	
(R <sub>6</sub> ,r <sub>1</sub> )	0.076		(R <sub>6</sub> ,r <sub>1</sub> )	0.077	
(r <sub>1</sub> ,r <sub>1</sub> )	5.113		(r <sub>1</sub> ,r <sub>1</sub> )	5.115	
(R <sub>4</sub> ,r <sub>3</sub> )	0.075		(R <sub>4</sub> ,r <sub>3</sub> )	0.076	
(R <sub>5</sub> ,r <sub>3</sub> )	0.096		(R <sub>5</sub> ,r <sub>3</sub> )	0.093	
(r <sub>3</sub> ,r <sub>3</sub> )	5.153		(r <sub>3</sub> ,r <sub>3</sub> )	5.155	
			(R <sub>7</sub> ,r <sub>5</sub> )	0.092	
			(R <sub>8</sub> ,r <sub>5</sub> )	0.092	
			(r <sub>5</sub> ,r <sub>5</sub> )	5.085	

C-C coupling								
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	R <sub>7</sub>	R <sub>8</sub>
R <sub>1</sub> (nap)	6.076	0.586	-0.332	0.301	-0.438	0.608	0.705	-0.169
R <sub>1</sub> (anth)	5.695	0.442	-0.241	0.217	-0.363	0.529	0.769	-0.253
r <sub>1</sub> (nap)	0.060	-0.015	-0.020	-0.016	0.002	0.076	0.003	0.004
r <sub>1</sub> (anth)	0.057	-0.015	-0.019	-0.016	0.001	0.077	0.004	0.007
$\beta_1$ (nap)	-0.183	0.001	0.017	-0.019	0.005	0.164	0.018	0.001
$\beta_1$ (anth)	-0.183	0.005	0.016	-0.017	0.003	0.167	0.018	0.000
	R <sub>9</sub>	R <sub>10</sub>	R <sub>11</sub>	R <sub>12</sub>	R <sub>13</sub>	R <sub>14</sub>	R <sub>15</sub>	R <sub>16</sub>
R <sub>1</sub> (nap)	0.073	-0.251	0.135					
R <sub>1</sub> (anth)	0.025	-0.193	0.141	0.103	-0.047	0.053	-0.051	0.042
r <sub>1</sub> (nap)	0.005	0.013	-0.001					
r <sub>1</sub> (anth)	0.005	0.008	-0.002	0.000	0.002	-0.002	0.001	-0.001
$\beta_1$ (nap)	-0.006	0.000	-0.004					
$\beta_1$ (anth)	-0.006	0.000	-0.003	-0.001	0.000	0.000	0.000	0.000

C-H coupling								
	r <sub>1</sub>	r <sub>2</sub>	r <sub>3</sub>	r <sub>4</sub>	r <sub>5</sub>	r <sub>6</sub>	r <sub>7</sub>	r <sub>8</sub>
r <sub>1</sub> (nap)	5.113	0.002	0.004	0.011	0.013	0.001	0.000	0.002
r <sub>1</sub> (anth)	5.115	0.002	0.004	0.011	0.011	0.002	0.000	0.000
	r <sub>9</sub>	r <sub>10</sub>						
r <sub>1</sub> (anth)	0.000	0.000						

\*stretch,bend and stretch-bend constants are in mdyn/Å,mdynÅ/rad and mdyn/rad respectively.

Table 4.4: Fitted ab initio(4-21G) frequencies of naphthalene

Symmetry blocks	present work		SQM <sup>a</sup>		HF/6-31G <sup>*b</sup> scaled(d <sub>0</sub> )	Experiment <sup>a</sup>		PED
	d <sub>0</sub>	d <sub>8</sub>	d <sub>0</sub>	d <sub>8</sub>		d <sub>0</sub>	d <sub>8</sub>	
A <sub>1g</sub>	3079	2285	3085	2289	3085	3060	2291	r <sub>3</sub> +r <sub>1</sub>
	3053	2253	3056	2257	3056	3031	2257	r <sub>1</sub> +r <sub>3</sub>
	1579	1554	1590	1563	1645	1578	1553	R <sub>4</sub> +R <sub>5</sub> + $\delta_2$
	1461	1292	1458	1287	1453	1460	1298	$\beta_1+\beta_2$ +R <sub>5</sub>
	1384	1381	1385	1385	1355	1380	1386	R <sub>2</sub> +R <sub>1</sub> +R <sub>4</sub>
	1166	837	1170	838	1134	1163	835	$\beta_2+\beta_1$
	1023	861	1023	860	1043	1020	863	R <sub>5</sub> + $\beta_1$ +R <sub>4</sub>
	762	691	757	689	780	761	692	R <sub>1</sub> +R <sub>2</sub> + $\delta_2$
	513	494	505	486	517	514	493	$\delta_2$ +R <sub>1</sub>
B <sub>3g</sub>	3063	2270	3067	2273	3069	3055	2276	r <sub>3</sub> +r <sub>1</sub>
	3046	2249	3047	2246	3046	(3055) <sup>c</sup>	2257	r <sub>1</sub> +r <sub>3</sub>
	1632	1602	1644	1617	1673	1624	1605	R <sub>4</sub> +R <sub>1</sub> + $\beta_1$
	1455	1355	1458	1359	1461	1458	1353	$\beta_2$ +R <sub>1</sub> +R <sub>4</sub>
	1245	828	1255	833	1219	1240	828	$\beta_1$ +R <sub>1</sub> + $\delta_1$
	1153	1024	1156	1030	1149	1158	1027	$\beta_2+\beta_1$ +R <sub>4</sub>
	940	882	940	879	917	939	883	$\delta_1$
	508	491	512	495	491	508	491	$\delta_3$
B <sub>1u</sub>	3066	2274	3070	2275	3071	3056	2295	r <sub>3</sub> +r <sub>1</sub>
	3050	2252	3049	2249	3047	3029	2278	r <sub>1</sub> +r <sub>3</sub>
	1594	1546	1595	1546	1654	1595	1545	R <sub>4</sub> + $\beta_2$
	1395	1254	1391	1248	1364	1389	1260	$\beta_2+\beta_1$ +R <sub>1</sub>
	1271	1044	1272	1049	1261	1265	1045	$\beta_1$ +R <sub>1</sub> + $\delta_1$
	1129	887	1137	882	1130	1125	885	$\delta_1+\beta_2$ +R <sub>4</sub> + $\beta_1$
	805	740	792	737	781	810	734	$\delta_1+\delta_3$ +R <sub>1</sub>
	358	327	354	323	364	359	326	$\delta_3$ +R <sub>1</sub>
B <sub>2u</sub>	3077	2284	3083	2288	3083	3056	2295	r <sub>3</sub> +r <sub>1</sub>
	3048	2250	3052	2253	3052	3029	2258	r <sub>1</sub> +r <sub>3</sub>
	1509	1446	1515	1446	1539	1509	1445	R <sub>5</sub> + $\beta_2$ +R <sub>1</sub> + $\beta_1$
	1354	1294	1341	1288	1321	1361	1290	R <sub>4</sub> + $\beta_1$
	1208	1090	1204	1081	1165	1209	1089	R <sub>1</sub> + $\beta_2$
	1154	839	1158	840	1091	1163	840	$\beta_1$ +R <sub>1</sub> + $\beta_2$ +R <sub>4</sub>
	1008	827	1002	826	988	1008	828	R <sub>5</sub> +R <sub>4</sub> + $\beta_1$
	620	593	626	600	596	619	594	$\delta_2$
A <sub>1u</sub>	975	816	981	815	970	970	—	$\gamma_3+\gamma_1$
	837	657	825	647	824	841	—	$\gamma_1+\gamma_3$
	591	501	622	531	606	581	—	$\tau_1+\gamma_1$
	190	171	188	169	184	195	—	$\tau_2+\tau_1$

Table 4.4: (Continued): Fitted frequencies of naphthalene

Symmetry blocks	present work		SQM <sup>a</sup>		HF/6-31G <sup>*b</sup> scaled(d <sub>0</sub> )	Experiment <sup>c</sup>		PED
	d <sub>0</sub>	d <sub>8</sub>	d <sub>0</sub>	d <sub>8</sub>		d <sub>0</sub>	d <sub>8</sub>	
B <sub>3u</sub>	962	790	969	797	977	958	791	$\tau_1 + \tau_3 + \tau_3$
	781	629	777	627	791	780	629	$\tau_3 + \tau_1$
	476	401	480	404	485	476	401	$\tau_1 + \tau + \tau_3$
	166	153	172	159	172	166	153	$\tau + \tau_3$
B <sub>1g</sub>	954	762	952	761	968	951	766	$\tau_1 + \tau_3$
	712	538	705	532	708	717	541	$\tau_3 + \tau_1$
	392	345	387	341	397	386	350	$\tau_3 + \tau_3$
B <sub>2g</sub>	992	871	987	857	985	983	875	$\tau_3 + \tau_1 + \tau_1 + \tau$
	887	758	879	766	880	876	761	$\tau_1 + \tau_3$
	772	635	773	634	785	772	646	$\tau_1 + \tau_2$
	472	417	471	413	478	470	413	$\tau_2 + \tau_1 + \tau_3$
Ave. error	[5.7]	[4.0]	incl.	C-H				
Ave. error	[3.6]	[2.4]	excl.	C-H				

a. Ref 3.

b. Ref 2.

c. Number in the parenthesis is not used in fitting.

Table 4.5: Anharmonic and harmonic frequencies and force constants of C-H and C-D vibrations of naphthalene and anthracene

Naphthalene					
Symmetry blocks	Anharmonic		Expt [3]	Harmonic	
	C <sub>10</sub> D <sub>8</sub>	C <sub>10</sub> H <sub>8</sub>		C <sub>10</sub> D <sub>8</sub>	C <sub>10</sub> H <sub>8</sub>
A <sub>1g</sub>	2291	3060	3060	2350	3177
	2257	3034	3031	2315	3150
B <sub>3g</sub>	2276	3046	3055	2334	3162
	2257	3031	(3055)	2315	3146
B <sub>1u</sub>	2295	3048	3056	2354	3164
	2278	3034	3029	2336	3150
B <sub>2u</sub>	2295	3058	3056	2354	3175
	2258	3030	3029	2316	3145
<i>f</i> <sub>C-H<sub>α</sub></sub>	5.113	—	—	5.459	—
<i>f</i> <sub>C-H<sub>β</sub></sub>	5.153	—	—	5.486	—

Anthracene			
Symmetry blocks	Harmonic	Anharmonic	Expt
	C <sub>14</sub> H <sub>10</sub>	C <sub>14</sub> H <sub>10</sub>	[19]
A <sub>1g</sub>	3177	3079	3072
	3150	3052	3048
	3141	3040	3027
B <sub>3g</sub>	3164	3066	3054
	3149	3049	3017
B <sub>1u</sub>	3165	3066	3084
	3150	3050	3052
	3150	3050	3052
B <sub>2u</sub>	3143	3042	3022
	3176	3079	3067
	3148	3051	3021
<i>f</i> <sub>C-H<sub>α</sub></sub>	5.461	5.115	
<i>f</i> <sub>C-H<sub>β</sub></sub>	5.489	5.155	
<i>f</i> <sub>C-H</sub>	5.429	5.085	

Table 4.6: Predicted vibrational frequencies of anthracene

Symmetry blocks	Benzene G.M <sup>a</sup>	Naphthalene G.M <sup>a</sup>	All <sup>b</sup>	Expt <sup>c</sup>	PED
A <sub>1g</sub>	-19	-8	-7	3072	$r_3+r_1$
	-15	-4	-4	3048	$r_1+r_3$
	-28	-17	-13	3027	$r_5$
	-28	-9	-3	1561	$R_4+R_2+R_5+R_7$
	3	-10	-4	1480	$R_5+\beta_1+\beta_1+R_7$
	-9	6	4	1412	$R_2+R_4+R_1+R_7$
	4	-11	-21	1264	$R_1+R_7+\beta_1$
	-15	-11	-8	1164	$\beta_1+\beta_1$
	13	1	8	1007	$R_5+R_4+\beta_1$
	1	9	5	754	$R_1+\alpha_2+R_7+R_1$
	3	0	-1	625	$\beta_1$
	8	3	0	397	$\alpha_2+R_7+R_1$
B <sub>3g</sub>	-22	-11	-12	3054	$r_3+r_1$
	-39	-28	-32	3017	$r_1+r_3$
	-37	-46	-2	1632	$R_4+R_7+R_1$
	-24	-22	0	1596	$R_7+R_4$
	-2	-4	-4	1384 <sup>d</sup>	$\beta_1+\beta_1+R_1$
	-13	-13	-20	1273	$\beta_5+\beta_1$
	-11	-8	0	1187	$\beta_1+\beta_5+R_1$
	-1	-6	-1	1098	$R_1+\beta_1+R_4$
	-13	-20	-13	903	$\delta_1$
	1	-2	-2	522	$\delta_3$
B <sub>1u</sub>	10	7	9	397	$\delta_2$
	7	18	18	3084	$r_3+r_1$
	-5	6	2	3052	$r_1+r_3+r_5$
	-30	-20	-20	3022	$r_5+r_1$
	-44	-30	-9	1627	$R_4+R_1$
	-7	-18	-7	1450	$\beta_1+R_1+R_7$
	24	13	6	1346	$R_7+\delta_1+\beta_1$
	5	0	1	1272	$\beta_1+\alpha_2+R_1$
	-12	-7	-4	1151	$\beta_1+\beta_1+R_4$
	1	-5	-4	908	$\delta_1$
B <sub>2u</sub>	7	0	7	652	$\delta_3+\delta_1+R_1$
	5	3	2	234	$\delta_3+R_7$
	-24	-12	-12	3067	$r_3+r_1$
	-40	-29	-30	3021	$r_1+r_3$
	-28	-23	-18	1542	$R_4+R_5+R_7$
	10	8	15	1460	$\beta_1+\beta_1+R_5+R_1$
	-7	13	-4	1400	$R_2+\beta_5+R_1+R_4$

Table 4.6: (Continued): Predicted frequencies of anthracene

Symmetry blocks	Benzene G.M <sup>a</sup>	Naphthalene G.M <sup>a</sup> All <sup>b</sup>		Expt <sup>c</sup>	PED
A <sub>1u</sub>	35	38	33	1318	R <sub>7</sub> +β <sub>5</sub> +β <sub>1</sub>
	-2	1	0	1167	β <sub>3</sub> +R <sub>1</sub> +β <sub>5</sub>
	38	31	-13	1124	R <sub>7</sub> +β <sub>1</sub> +R <sub>4</sub>
	19	5	5	998	R <sub>5</sub> +β <sub>1</sub>
	16	18	13	809	R <sub>1</sub> +R <sub>2</sub>
	6	4	1	603	δ <sub>2</sub>
	-11	-6	4	988	γ <sub>3</sub> +γ <sub>1</sub>
	17	18	3	858	γ <sub>1</sub> +γ <sub>3</sub>
	-6	5	4	743	τ <sub>1</sub> +τ <sub>2</sub>
	7	-9	0	(491) <sup>f</sup>	τ <sub>2</sub> +γ <sub>1</sub> +τ <sub>1</sub>
B <sub>3u</sub>	9	3	0	126	τ <sub>2</sub> +τ <sub>1</sub>
	-18	-26	-12	958	γ <sub>1</sub> +γ <sub>3</sub> +τ <sub>3</sub>
	-17	-20	-16	879	γ <sub>5</sub> +τ <sub>3</sub> +γ <sub>3</sub>
	12	14	5	726	γ <sub>1</sub> +γ <sub>3</sub> +γ <sub>5</sub>
	7	8	4	469	τ <sub>1</sub> +τ <sub>2</sub> +τ <sub>3</sub>
	14	4	-1	380	τ <sub>3</sub>
B <sub>1g</sub>	19	19	19	106	τ <sub>1</sub> +τ <sub>2</sub> +τ <sub>3</sub>
	-14	-22	-8	956	γ <sub>1</sub> +γ <sub>3</sub> +τ <sub>3</sub>
	16	20	9	760	γ <sub>1</sub> +γ <sub>3</sub>
	11	12	8	479	τ <sub>1</sub> +τ <sub>2</sub> +τ <sub>3</sub>
	22	20	21	244	τ <sub>3</sub> +τ <sub>1</sub> +τ <sub>2</sub>
B <sub>2g</sub>	-23	-19	-9	977	γ <sub>3</sub> +γ <sub>1</sub>
	1	7	0	916	γ <sub>5</sub> +γ <sub>3</sub>
	29	36	21	852 <sup>e</sup> , 896	γ <sub>1</sub> +γ <sub>3</sub> +γ <sub>5</sub>
	-9	24	16	773	τ <sub>1</sub>
	6	21	29	580	τ <sub>1</sub> +γ <sub>1</sub> +τ <sub>2</sub>
	29	22	24	287	τ <sub>2</sub> +τ <sub>1</sub>
Ave.error	[15.0]	[13.5]	[9.2]	including CH	
Ave.error	[13.6]	[13.2]	[8.2]	excluding CH	

a. Geometric mean of the respective diagonal scale factors are taken for the off-diagonal scale factors.

b. All(diagonal and off-diagonal) scale factors are taken.

c. Ref. 19.

d. Ref. 23.

e. Ref. 26.

f. Number in the parenthesis is our predicted frequency.

Table 4.7: Orthogonal transformation matrix of naphthalene

In-plane									
1	1	0.5000	3	0.5000	7	0.5000	11	0.5000	
2	2	1.0000							
3	4	0.5000	6	0.5000	8	0.5000	10	0.5000	
4	5	0.7071	9	0.7071					
5	12	0.5000	13	0.5000	16	0.5000	19	0.5000	
6	14	0.5000	15	0.5000	17	0.5000	18	0.5000	
7	20	0.5000	21	-0.5000	24	-0.5000	27	0.5000	
8	22	0.5000	23	-0.5000	25	0.5000	26	-0.5000	
9	29	0.7071	32	0.7071					
10	1	0.5000	3	-0.5000	7	-0.5000	11	0.5000	
11	4	0.5000	6	-0.5000	8	0.5000	10	-0.5000	
12	12	0.5000	13	-0.5000	16	-0.5000	19	0.5000	
13	14	0.5000	15	-0.5000	17	0.5000	18	-0.5000	
14	20	0.5000	21	0.5000	24	0.5000	27	0.5000	
15	22	0.5000	23	0.5000	25	0.5000	26	0.5000	
16	28	0.7071	31	-0.7071					
17	30	0.7071	33	0.7071					
18	1	0.5000	3	0.5000	7	-0.5000	11	-0.5000	
19	4	0.5000	6	0.5000	8	-0.5000	10	-0.5000	
20	5	0.7071	9	-0.7071					
21	12	0.5000	13	0.5000	16	-0.5000	19	-0.5000	
22	14	0.5000	15	0.5000	17	-0.5000	18	-0.5000	
23	20	0.5000	21	-0.5000	24	0.5000	27	-0.5000	
24	22	0.5000	23	-0.5000	25	-0.5000	26	0.5000	
25	29	0.7071	32	-0.7071					
26	1	0.5000	3	-0.5000	7	0.5000	11	-0.5000	
27	4	0.5000	6	-0.5000	8	-0.5000	10	0.5000	
28	12	0.5000	13	-0.5000	16	0.5000	19	-0.5000	
29	14	0.5000	15	-0.5000	17	-0.5000	18	0.5000	
30	20	0.5000	21	0.5000	24	-0.5000	27	-0.5000	
31	22	0.5000	23	0.5000	25	-0.5000	26	-0.5000	
32	28	0.7071	31	0.7071					
33	30	0.7071	33	-0.7071					
Out-of-plane									
1	1	0.5000	2	-0.5000	5	0.5000	8	-0.5000	
2	3	0.5000	4	-0.5000	6	-0.5000	7	0.5000	
3	9	0.7071	12	-0.7071					
4	10	0.7071	13	-0.7071					
5	1	0.5000	2	0.5000	5	-0.5000	8	-0.5000	



Table 4.7: (Continued): Orthogonal matrix of naphthalene

6	3	0.5000	4	0.5000	6	-0.5000	7	-0.5000
7	11	0.7071	14	-0.7071				
8	1	0.5000	2	-0.5000	5	-0.5000	8	0.5000
9	3	0.5000	4	-0.5000	6	0.5000	7	-0.5000
10	9	0.7071	12	0.7071				
11	10	0.7071	13	0.7071				
12	1	0.5000	2	0.5000	5	0.5000	8	0.5000
13	3	0.5000	4	0.5000	6	0.5000	7	0.5000
14	11	0.7071	14	0.7071				
15	15	1.0000						

Table 4.8: Orthogonal transformation matrix of anthracene

In-plane								
1	1	0.5000	3	0.5000	12	0.5000	16	0.5000
2	2	0.7071	9	0.7071				
3	4	0.5000	6	0.5000	13	0.5000	15	0.5000
4	5	0.7071	14	0.7071				
5	7	0.5000	8	0.5000	10	0.5000	11	0.5000
6	17	0.5000	18	0.5000	23	0.5000	26	0.5000
7	19	0.5000	20	0.5000	24	0.5000	25	0.5000
8	21	0.7071	22	0.7071				
9	27	0.5000	28	-0.5000	33	-0.5000	36	0.5000
10	29	0.5000	30	-0.5000	34	0.5000	35	-0.5000
11	38	0.7071	44	0.7071				
12	41	1.0000						
13	1	0.5000	3	-0.5000	12	-0.5000	16	0.5000
14	4	0.5000	6	-0.5000	13	0.5000	15	-0.5000
15	7	0.5000	8	-0.5000	10	0.5000	11	-0.5000
16	17	0.5000	18	-0.5000	23	-0.5000	26	0.5000
17	19	0.5000	20	-0.5000	24	0.5000	25	-0.5000
18	27	0.5000	28	0.5000	33	0.5000	36	0.5000
19	29	0.5000	30	0.5000	34	0.5000	35	0.5000
20	31	0.7071	32	0.7071				
21	37	0.7071	43	-0.7071				
22	39	0.7071	45	0.7071				
23	42	1.0000						
24	1	0.5000	3	0.5000	12	-0.5000	16	-0.5000
25	2	0.7071	9	-0.7071				
26	4	0.5000	6	0.5000	13	-0.5000	15	-0.5000

Table 4.8: (Continued): Orthogonal matrix of anthracene

27	5	0.7071	14	-0.7071					
28	7	0.5000	8	-0.5000	10	-0.5000	11	0.5000	
29	17	0.5000	18	0.5000	23	-0.5000	26	-0.5000	
30	19	0.5000	20	0.5000	24	-0.5000	25	-0.5000	
31	27	0.5000	28	-0.5000	33	0.5000	36	-0.5000	
32	29	0.5000	30	-0.5000	34	-0.5000	35	0.5000	
33	31	0.7071	32	-0.7071					
34	38	0.7071	44	-0.7071					
35	1	0.5000	3	-0.5000	12	0.5000	16	-0.5000	
36	4	0.5000	6	-0.5000	13	-0.5000	15	0.5000	
37	7	0.5000	8	0.5000	10	-0.5000	11	-0.5000	
38	17	0.5000	18	-0.5000	23	0.5000	26	-0.5000	
39	19	0.5000	20	-0.5000	24	-0.5000	25	0.5000	
40	21	0.7071	22	-0.7071					
41	27	0.5000	28	0.5000	33	-0.5000	36	-0.5000	
42	29	0.5000	30	0.5000	34	-0.5000	35	-0.5000	
43	37	0.7071	43	0.7071					
44	39	0.7071	45	-0.7071					
45	40	1.0000							

## Out-of-plane

1	1	0.5000	2	-0.5000	7	0.5000	10	-0.5000	
2	3	0.5000	4	-0.5000	8	-0.5000	9	0.5000	
3	5	0.7071	6	-0.7071					
4	11	0.7071	17	-0.7071					
5	12	0.7071	18	-0.7071					
6	14	1.0000							
7	1	0.5000	2	0.5000	7	-0.5000	10	-0.5000	
8	3	0.5000	4	0.5000	8	-0.5000	9	-0.5000	
9	13	0.7071	19	-0.7071					
10	20	0.7071	21	-0.7071					
11	1	0.5000	2	-0.5000	7	-0.5000	10	0.5000	
12	3	0.5000	4	-0.5000	8	0.5000	9	-0.5000	
13	11	0.7071	17	0.7071					
14	12	0.7071	18	0.7071					
15	15	1.0000							
16	1	0.5000	2	0.5000	7	0.5000	10	0.5000	
17	3	0.5000	4	0.5000	8	0.5000	9	0.5000	
18	5	0.7071	6	0.7071					
19	13	0.7071	19	0.7071					
20	16	1.0000							
21	20	0.7071	21	0.7071					



Table 4.9: (Continued): Naphthalene in plane symbolic F matrix in loc 1 coordinates

136	0-136	137	0-137	138	139	0-139-138	140-140	141-141	142	143-143-	142	144
144	145	145	146	147	147	146	148	0	149			
109	0-109-110	0	110	107-108	0	108-107	113-113-114	114	111-112	112-1	1	117
-117-118-118-115-116-116-115	150	0	151	119								
124	121	124	125	126	125	120	122	123	122	120	129	129
133	134-134-131	132-132	131	0	152	0	0	135				
-138	0	138	139	0-139-136	137	0-137	136-142	142	143-143-140	141-141	1	0
146	147	147	144	145	145	144-151	0	153-148	0	149		

Fitted in plane force constants of naphthalene

6.076	0.586	5.607	-0.332	0.301	-0.226	0.608	7.513	-0.438	0	75
0.647	6.112	-0.362	0.705	0.135	-0.251	0.073	-0.169	0.139	-0	08
0.150	0.242	0.060	-0.015	-0.020	-0.016	0.002	0.076	0.003	0	04
0.005	0.013	-0.001	5.113	0.002	-0.027	-0.024	-0.006	0.075	0	96
-0.003	0.000	0.000	-0.003	0.001	0.005	0.004	0.011	5.153	0	11
0.013	0.002	0.000	0.001	0.000	0.001	-0.183	0.001	0.017	-0	19
0.005	0.164	0.018	0.001	-0.006	0.000	-0.004	0.003	0.000	0	06
-0.006	-0.010	0.000	0.000	-0.002	0.503	-0.001	0.021	-0.011	0	08
0.178	-0.159	-0.008	-0.001	-0.001	-0.004	0.003	0.005	-0.006	-0	08
0.005	0.004	0.001	0.000	0.001	0.000	-0.009	0.008	0.506	0	07
-0.003	0.003	0.001	0.000	0.000	-0.001	0.124	-0.035	0.286	0	02
-0.094	-0.088	-0.006	0.005	-0.001	-0.002	0.008	0.011	1.426	0	07
-0.112	0.071	-0.426	0.147	-0.032	-0.154	-0.094	0.044	-0.014	0	07
0.003	0.061	-0.009	0.005	1.332	0.080	0.308	-0.221	-0.055	0	05
-0.072	0.008	-0.005	-0.071	0.052	-0.008	-0.010	-0.188	1.358	0	07
-0.291	0.247	-0.303								

\* The non-redundant local coordinates are as given in Table-4.1.



Table 4.11: Anthracene in plane symbolic F matrix in non-redundant local coordinates

[illegible]

Table 4.11: (Continued): Anthracene in plane symbolic F matrix in local coordinates

159	160	161	162	163	164	165-165-160	166-166-159-164-163-162-161	167	168	169	170
0	0-167-170-169-168	171	172	173	174	175					
-161-160-159-164-163-162	166-166	160	165-165	161	162	163	164	159-168-167-170-169			
0	0	168	169	170	167	172	171	174	173	176	175
-112-109-116-115-114-113-108-107-102-111-110-101-106-105-104-103-123-126-125-124											
-121-122-117-120-119-118	177	178	179	180	171	172	127				
144	137	140	141	142	143	138	139	130	135	136	131
150	149	146	147	148	145	180	179	181	182	174	173
-140-137-144-143-142-141-136-135-130-139-138-129-134-133-132-131-151-154-153-152											
-149-150-145-148-147-146	179	180	182	181	173	174	155	158	157		
116	109	112	113	114	115	110	111	102	107	108	103
122	121	118	119	120	117	178	177	180	179	172	171
183	0-183	184	0-184	185	186	0-186-185	187	188	0-188-187	189-189	190-190
191-191	192	193-193-192	194	194	195	195	196	196	197	198	198
200	201	200	202	203	202	204	205	206	205	204	207
212	212	213	214	214	213	215-215	216-216	217-217	218	219-219-218	0
221	0-221	222	0-222	223	224	0-224-223	225	226	0-226-225	227-227	228-228
229-229	230	231-231-230	232	232	233	233	234	234	235	236	236
239	0-239	240	0-240	241	241	0-241-241	239-240	0	240-239	242-242	243-243
244-244	242-243	243-242	245	245	246	246	0	0-245-246-246-245	247	0	248
250	251	250	252	253	252	254	254	251	254	254	250
257	257	255	256	256	255	258-258	259-259	0	0-258	259-259	258
261											
262	0-262	263	0-263	264-264	0	264-264-262	263	0-263	262	265-265	266-266
0	0-265	266-266	265	267	267	268	268	269	269	267	268
0	272										
187	0-187-188	0	188	186	185	0-185-186	183-184	0	184-183	192-192-193	193
191-191	189-190	190-189-197-197-198-198-196-196-194-195-195-194	273	0	274	247					
0-270	199										
207	206	207	208	209	208	205	204	201	204	205	200
212	212	210	211	211	210-218	218	219-219-217	217-215	216-216	215	0
260	0	0	220								
-225	0	225	226	0-226-224-223	0	223	224-221	222	0-222	221-230	230
-229	229-227	228-228	227	235	235	236	236	234	234	232	233
0	271-237	0	238								

Table 4.11: (Continued): Anthracene in plane symbolic F matrix in local coordinates

Scaled in plane force constants of anthracene

5.695	0.442	5.242	-0.241	0.217	-0.126	0.529	7.988	-0.363	0.067
0.579	5.703	-0.291	0.769	0.728	0.141	-0.263	0.098	-0.194	7.019
-0.253	-0.432	-0.193	0.144	-0.125	0.157	0.785	0.025	0.105	0.062
0.167	0.279	-0.394	0.103	0.042	-0.051	0.053	-0.047	0.046	0.048
0.039	0.069	0.057	-0.015	-0.019	-0.016	0.001	0.077	0.004	0.007
0.005	0.008	-0.002	0.000	0.002	-0.002	0.001	-0.001	5.115	0.002
-0.026	-0.024	-0.007	0.076	0.093	-0.002	0.000	0.000	-0.003	0.001
0.005	0.000	0.001	-0.001	0.001	0.000	0.004	0.011	5.155	0.011
0.000	-0.011	-0.001	0.009	0.007	0.004	0.092	-0.017	0.011	0.002
0.000	0.001	5.085	0.003	0.000	0.000	0.000	0.000	0.000	0.000
-0.183	0.005	0.016	-0.017	0.003	0.167	0.018	0.000	-0.006	0.000
-0.003	-0.001	0.000	0.000	0.000	0.000	0.005	0.000	0.006	-0.006
-0.010	-0.003	0.000	0.000	0.000	0.000	0.502	-0.001	0.019	-0.010
0.007	0.181	-0.159	-0.008	-0.002	0.000	-0.003	0.004	0.005	-0.001
0.001	-0.001	0.001	0.000	-0.006	-0.009	0.008	0.004	0.001	0.001
0.000	0.000	0.000	0.000	-0.009	0.008	0.506	0.007	-0.014	-0.001
0.004	-0.001	0.004	-0.001	0.209	0.016	0.010	0.003	0.000	0.000
-0.004	0.004	0.001	0.000	0.511	-0.001	0.000	0.000	0.000	0.000
0.000	0.000	0.132	-0.035	0.294	0.096	0.008	0.004	-0.093	-0.087
-0.006	0.000	0.001	0.000	-0.002	0.009	-0.001	0.001	1.429	0.287
-0.090	0.066	-0.422	0.148	-0.031	-0.176	0.004	0.003	-0.009	-0.093
0.045	-0.011	0.002	0.002	0.003	0.061	-0.006	0.001	0.001	1.316
0.058	0.285	-0.223	-0.057	-0.005	0.002	0.004	-0.072	0.008	-0.001
0.000	-0.070	0.051	-0.008	-0.001	-0.001	-0.192	1.327	0.290	-0.069
0.147	-0.005	-0.005	-0.101	-0.008	-0.012	0.324	-0.282	1.583	0.154
-0.235	-0.036	-0.154	0.231	-0.013	0.007	-0.148	0.010	0.006	0.250
1.468	0.222	-0.056	-0.109	-0.009	-0.004	-0.008	-0.010	-0.077	0.294
-0.308	1.527	0.016	-0.012	0.011	0.005				

\* Non-redundant local coordinates are as given in Table-4.2.





Table 4.13: Mean amplitudes of vibration(A) of naphthalene

parameter*	calc.	[ref.32]	[ref.33]	parameter*	calc.	[ref.32]	[ref.33]
14-18	0.160	0.159	0.159	10-12	0.132	0.133	0.133
14-17	0.131	0.134	0.134	2-15	0.094	0.095	0.095
12-18	0.168	0.159	0.159	6-11	0.106	0.108	0.108
14-12	0.188	0.188	0.188	10-11	0.124	0.123	0.123
14-16	0.168	0.171	0.171	6-15	0.097	0.099	0.099
14-13	0.119	0.119	0.119	10-16	0.102	0.107	0.107
14-11	0.130	0.133	0.133	10-15	0.099	0.101	0.101
14-15	0.145	0.145	0.145	6-10	0.044	0.047	0.047
18-16	0.135	0.141	0.141	1-2	0.047	0.047	0.047
18-15	0.123	0.125	0.125	2-6	0.047	0.048	0.047
6-14	0.077	0.077	0.076	10-9	0.047	0.048	0.047
10-14	0.101	0.100	0.097	2-10	0.054	0.056	0.058
6-18	0.098	0.100	0.097	6-9	0.056	0.056	0.058
2-14	0.099	0.101	0.098	2-5	0.056	0.057	0.060
10-17	0.099	0.101	0.098	3-5	0.060	0.065	0.068
6-12	0.132	0.132	0.132	2-9	0.062	0.061	0.070
6-17	0.094	0.097	0.098	6-5	0.063	0.060	0.070
2-18	0.095	0.097	0.097	6-8	0.062	0.068	0.072
10-13	0.096	0.098	0.098	6-3	0.060	0.064	0.068
2-13	0.096	0.098	0.098	6-7	0.066	0.067	0.077
2-17	0.094	0.095	0.098	8-10	0.063	0.068	0.078
6-13	0.095	0.095	0.095	7-10	0.066	0.068	0.078

\*Atom numberings are according to Figure 4.1.

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## Chapter 5

# Theoretical Prediction of Vibrational Spectrum of N-Glycylglycine Hydrochloride

In this chapter, theoretical prediction of the vibrational spectrum of the smallest dipeptide hydrochloride from its parent amino acid frequencies is presented by transferring the complete set of scale factors obtained by using the fitting procedure described in chapter 3.

The scaled quantum mechanical (SQM) approach proved to be very successful for a large number of symmetric organic molecules [1,2]. However the success is limited when the SQM procedure is applied to amino acids. Since there is no symmetry in the amino acids (point group  $C_1$ ), each force constant is different from the other and many set of scale factors give equally good fit and hence becomes difficult to obtain a unique solution [3]. Also, equally difficult problem is that the ab initio PEDs are different from the experimentally obtained PEDs implying that the ab initio result of isolated molecule is a poor model for amino acids in condensed phase [4]. This is because the ab initio calculation of isolated zwitterion either goes to neutral gas phase spectrum [5] or even when it retains the geometry exhibits intramolecular H-bonding which is absent in the solution or solid state [4,6]. Attempts are being made to improve the model by explicitly including water molecules in the calculation (supermolecular calculation) or implicitly by introducing a dielectric medium (Onsager reaction field) [3,7-15]. SQM force field calculation on glycine cation supermolecule is available for cis and trans conformations

at HF/4-31G\* level [3]. Such supermolecular calculations although aimed at building a generalized scale factors for peptides, are difficult to extend to higher systems because of the increase in the number of atoms included as water molecules. Also the PEDs of water molecules get mixed up with amino acid vibrations and difficult to separate. Alanine zwitterion is studied by the reaction field approach in water environment [14]. This improves the ab initio model of isolated molecule although the agreement is not very good with the experimental PEDs.

An alternative solution to this problem could be the transfer of scale factors from smaller amino acids to the larger dipeptides for which the ab initio model correctly describes the gross features of experimental vibrational spectra. Ab initio calculations of isolated amino acids in their cationic or anionic forms (in acidic or basic solution) grossly resemble the experimental features because the intramolecular H-bonding is less pronounced in these molecules compared to their zwitterions. It appears that if the basis set is chosen carefully the intramolecular H-bonding problem could be reduced further. Hence, the present study involves a complete conformational and vibrational analysis of glycine hydrochloride (GH) and glycylglycine hydrochloride (GGH) and transfer of scale factors between them to obtain a reliable theoretical force field for the smallest dipeptide hydrochloride.

Many ab initio conformational and vibrational analyses of neutral amino acids are found in the literature [4,16-17]. To the best of our knowledge a complete ab initio vibrational analysis of any peptide is limited to our study of GGH [18]. An experimental Raman study of glycylglycine zwitterion (GG) and its normal mode analysis was reported by Lagant et al. [19].

## 5.1 Calculations

The geometry optimizations and frequency calculations for both GH and GGH were done using 4-21G and 6-31G\*\* basis sets. The ab initio force constants and frequencies of GH were calculated analytically and that of GGH numerically. The cartesian force constants of both GH and GGH were then transformed to the non-redundant local coordinates. The

non-redundant local coordinates of GH and GGH are shown in Table-5.1, Table-5.2 and Figure 5.1 and 5.2. The fitting procedure described in chapter 3 was used to get the scale factors for GH by fitting the frequencies of seven different isotopomers simultaneously. The fitting is extremely successful in producing an average deviation of  $9.7\text{ cm}^{-1}$  from the available experimental data. The ab initio force constants of GGH are scaled using the scale factors of GH. Durig's scaling procedure [20] was applied when there is no equivalent local symmetry coordinates between the two compounds. Durig's scaling involves using a scale factor of 0.9 for stretching, 0.8 for bending and their geometric mean for the off-diagonal ones. The experimental IR spectra of GGH was taken from our reported spectra [18]. Glycylglycine methyl ester hydrochloride (GGMH) was prepared by reacting  $\text{SOCl}_2$  with N-glycylglycine in methanol. The solution was dried under high vacuum. The IR spectrum was recorded using a Perkin-Elmer spectrophotometer.

## 5.2 Results

Amino acid hydrochlorides in solution dissociates into amino acid cation and  $\text{Cl}^-$  and hence, to a good approximation the spectral features could be accounted by the cation. Similar treatments were given successful results for other systems, for example, acetylcholine [21]. In solid state, each  $\text{Cl}^-$  is ionically bonded to the planar H-atom of the  $\text{N}^+\text{H}_3$  group with a bond distance of  $2.59\text{ \AA}$  in GH. The room temperature spectra of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$  are essentially identical, indicating that the anion has very small effect on the spectra [22]. The difference between the solid and solution phase spectra can be accounted in most cases to the phase change (mainly the strong intermolecular H-bonded network in the crystal structure vs. intermolecular H-bonding in a dielectric medium). Thus, as a reasonable approximation, the cations can be considered as a good theoretical model for the vibrational spectra of amino acid hydrochlorides and hence in the present study optimization and frequency calculations were performed with the respective cations of GH and GGH. Furthermore, the fully optimized structure of GH at HF/6-31G\*\* level of calculation by including  $\text{Cl}^-$  explicitly results in the dissociation of GH into neutral amino acid and HCl.



### 5.2.1 Conformations of GH

The conformational space of GH has been studied by several authors using *ab initio* theory. These studies clearly indicate that the lowest energy conformation is basis set dependent [23,24]. Since we are looking for a conformation in which the intramolecular H-bonding will be minimum so that it will mimic the solution or solid state spectra, we used 4-21G, a low level and 6-31G\*\*, a high level basis sets. For the present work we took only the two lowest energy conformations of GH from the earlier study [24]. At 4-21G level C1 is the lowest energy form whereas at 6-31G\*\*, C2 is the most stable one (Figure 5.3). Inclusion of correlation at the MP2 level does not improve 4-21G results while C2 changes to a structure closer to C1 at 6-31G\*\* level indicating that the HF/4-21G calculation reproduces the structure close to the global minima, though C2 is closer to the crystal structure [25]. In all the cases the frequency calculations on the optimized structure were done to make sure that they are real minima. Since the minimum energy conformation at HF/6-31G\*\* does not have the intramolecular H-bonding and also replicate the crystal structure, this basis set is used for the vibrational spectral study.

### 5.2.2 Conformations of GGH

Eight possible different conformations were selected by rotating the N-terminal and C-terminal groups of GGH. Each conformation is fully optimized at 6-31G\*\* basis set. The optimized structures are given in Figure 5.4 and the final results of different calculations are listed in Table-5.3. C1 is the minimum energy structure. Further MP2/6-31G\*\* single point calculations were performed to see the effect of correlation on the relative energies of these eight conformations. Frequency calculation was done only on the minimum energy conformation.

### 5.2.3 Vibrational Frequencies of GH

The solution phase IR and Raman spectra of several isotopomers of GH were reported by Williams et al. [3]. However, the supermolecular calculation with water molecules introduces strong coupling between the vibrational modes of GH and water. As a result regions below  $600\text{ cm}^{-1}$  are not very well described in their work. Also since the least

squares method does not lead to unique assignment, they constrained the scale factor in their SQM approach to yield PEDs that were in agreement with their empirical assignment. In the present work the fitting of the experimental frequencies of section 5.2 upon ours produced a better fit than that of Williams et al. except for the peak at  $568\text{ cm}^{-1}$  in GH  $\delta_0$ . For this mode the absolute deviation from the fitted one is  $30\text{ cm}^{-1}$ . It is possible that this frequency might have been misassigned. For all fundamentals the assignments are very close to that of unscaled ab initio normal modes. The PEDs of scaled force field are in good agreement with that of Williams et al. [3] and hence the assignment for GH will not be discussed further. The force field cannot be compared, as our results are based on isolated molecule. The fitted frequencies and their PEDs for GH-da are given in Table 5.4 and the corresponding fitted frequencies for the isotopomers are given in Table-5.5.

#### 5.2.4 Vibrational Frequencies of GGH

The frequencies obtained from the scaled force field and the corresponding PEDs of GGH are shown in Table-5.6. The predicted frequencies are in excellent agreement with the available experimental data with an average deviation of  $7.6\text{ cm}^{-1}$ . For a comparative study, the experimental frequencies of GG and GGMH are also given in the table.

The  $\nu\text{C=O}$  acid and  $\nu\text{C=O}$  amide bands are predicted at  $1738$  and  $1676\text{ cm}^{-1}$  and are observed at  $1746$  and  $1677\text{ cm}^{-1}$ . This is in agreement with the  $1724$  and  $1678\text{ cm}^{-1}$  bands of the corresponding GGMH. The  $\text{C=O}$  in acetic acid [3] is observed at  $1712\text{ cm}^{-1}$  and at  $1682\text{ cm}^{-1}$  in GG [19].

Both the  $\delta_a\text{N}^+\text{H}_3$  modes are predicted at  $1641$  and  $1602\text{ cm}^{-1}$  and are not observed in our IR spectra. However the  $1629$  and  $1611\text{ cm}^{-1}$  Raman bands of GG [19] are in very good agreement with our predicted numbers. These modes appear as degenerate bands at  $1607\text{ cm}^{-1}$  in GH in accordance with the prediction. The  $1648\text{ cm}^{-1}$  band and the weak shoulder at  $1622\text{ cm}^{-1}$  in the corresponding GGMH spectra compare well with these assignments. The asymmetric  $\text{NH}(\text{amide})$  bend is predicted at  $1593\text{ cm}^{-1}$  along with  $\nu\text{CN}$ ,  $\nu\text{C=O}(\text{amide})$  and  $\nu\text{NC}'$  is assigned to  $1584\text{ cm}^{-1}$ . This amide II mode is observed at a lower frequency ( $1531\text{ cm}^{-1}$ ) in the zwitterion. The  $1535\text{ cm}^{-1}$  band observed in the GGMH spectrum is in agreement with this assignment. The symmetric  $\text{N}^+\text{H}_3$  deformation is predicted at

1472  $\text{cm}^{-1}$  agrees very well with the 1480  $\text{cm}^{-1}$  in the zwitterionic spectra. This mode is assigned to the 1452  $\text{cm}^{-1}$  peak in the corresponding GGMH. Both the  $\rho\text{N}^+\text{H}_3$  modes are predicted at 1155 and 1126  $\text{cm}^{-1}$  and are observed at 1135 and 1117  $\text{cm}^{-1}$  in the GGH spectra, 1158 and 1100  $\text{cm}^{-1}$  in the zwitterion and 1130 and 1090  $\text{cm}^{-1}$  in the GGMH. In many amino acids these  $\rho\text{N}^+\text{H}_3$  modes appear as two closely spaced bands around 1100 to 1150  $\text{cm}^{-1}$  [26-28].

The observed band at 1487  $\text{cm}^{-1}$  is predicted very well at 1486  $\text{cm}^{-1}$  and is assigned to the mixed mode of  $\omega\text{C}'\text{H}_2$ ,  $\nu\text{C}'\text{C}$ ,  $\nu\text{C}-\text{O}$  and  $\omega\text{CH}_2$ . The various  $\text{CH}_2$  bending modes ( $\delta\text{CH}_2$ ,  $\omega\text{CH}_2$  and  $\text{tCH}_2$ ) are predicted at 1443, 1433, 1408, 1329 and 1242  $\text{cm}^{-1}$  and are assigned to the observed bands at 1434, 1434, 1410, 1308 and 1219  $\text{cm}^{-1}$  respectively. The 1447  $\text{cm}^{-1}$  Raman band assigned to  $\delta\text{CH}_2$  by Lagant et al. in the zwitterion spectra agrees very well with our predicted 1443  $\text{cm}^{-1}$  band. This mode is assigned to the observed band at 1437  $\text{cm}^{-1}$  in the GGMH. The  $\omega\text{CH}_2$  mode at 1408  $\text{cm}^{-1}$  is assigned to 1399 and 1402  $\text{cm}^{-1}$  in the corresponding GG and GGMH. The  $\text{CH}_2$  rocking modes are predicted at 1002 and 925  $\text{cm}^{-1}$ . Higher one is assigned to the observed band at 1013  $\text{cm}^{-1}$  and is consistent with the earlier assignment of Lagant et al. at 1007  $\text{cm}^{-1}$  in the zwitterionic spectra for this mode. Although there is no band corresponding to the lower one in our hydrochloride spectra this agrees well with the 918  $\text{cm}^{-1}$  band assignment of the zwitterionic spectra [19].

The predicted band at 1362  $\text{cm}^{-1}$  is assigned to  $\delta\text{COH}$  and  $\omega\text{C}'\text{H}_2$  is in agreement with the observed band at 1350  $\text{cm}^{-1}$ . This band is observed at 1378  $\text{cm}^{-1}$  in GH and is consistent with this assignment. There is no corresponding mode in the zwitterion spectra but appear at 1362  $\text{cm}^{-1}$  in the spectrum of GGMH. The  $\nu\text{N}^+\text{C}$  and one of the  $\nu\text{CC}' + \nu\text{CC}$  modes are predicted at 1050 and 907  $\text{cm}^{-1}$  are in excellent agreement with the observed bands of all the three compounds and also consistent with the 1044 and 873  $\text{cm}^{-1}$  bands of GH.

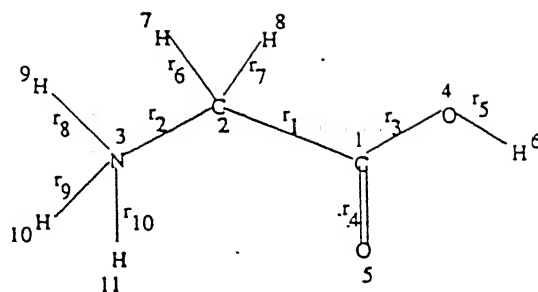
Bands predicted at 700 and 661  $\text{cm}^{-1}$  agree very well with the observed bands at 708 and 661  $\text{cm}^{-1}$  in the hydrochloride spectra, 708 and 665  $\text{cm}^{-1}$  in the zwitterion and 708 and 644  $\text{cm}^{-1}$  in the GGMH. Bands below 600  $\text{cm}^{-1}$  are not available for GGH and hence the predicted numbers below 600  $\text{cm}^{-1}$  are compared with the zwitterionic spectra of Lagant

et al. [19].

The optimized cartesian coordinates obtained by using 6-31G\*\* basis set for the minimum energy conformation of GH and GGH and their non-redundant scaled force constants are given in Table-5.7 to Table-5.10.

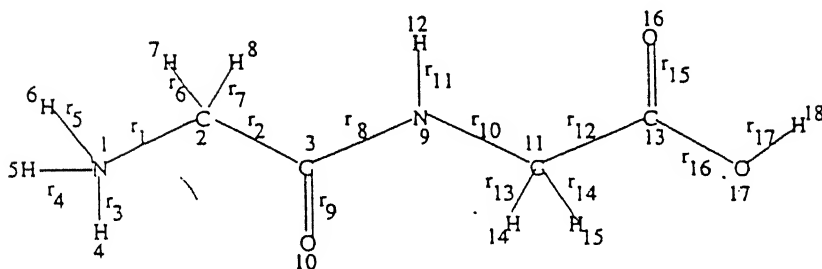
### 5.3 Conclusions

The fitting procedure to obtain the scale factors from the ab initio force field of GH has shown to be very successful giving an average deviation of  $9.7\text{cm}^{-1}$  between the predicted and the experimental frequencies for seven isotopomers. These scale factors when used to predict the frequencies of GGH the results were shown to be in good agreement with the experimental ones with an average deviation of  $7.6\text{cm}^{-1}$  for the smallest dipeptide hydrochloride. A complete set of non-redundant force constants were obtained for both GH and GGH. From the accuracy of the predicted frequencies it is clear that the methodology could, in principle, be used successfully for the prediction of vibrational frequencies and their force fields of larger polypeptides from their parent amino acids.



$$\begin{aligned}
 a_1 &= C_2 C_1 O_4, b_1 = C_2 C_1 O_5, b_2 = O_4 C_1 O_5, a_2 = C_1 O_4 H_6 \\
 a_3 &= H_7 C_2 H_8, a_4 = N_3 C_2 H_7, a_5 = N_3 C_2 H_8, b_3 = N_3 C_2 C_1 \\
 b_4 &= C_1 C_2 H_7, b_5 = C_1 C_2 H_8, a_6 = H_{10} N_3 H_{11}, a_7 = H_9 N_3 H_{10} \\
 a_8 &= H_9 N_3 H_{11}, b_6 = C_2 N_3 H_9, b_7 = C_2 N_3 H_{10}, b_8 = C_2 N_3 H_{11}
 \end{aligned}$$

Figure 5.1: Internal coordinates of GH.



$$\begin{aligned}
 a_1 &= H_5 N_1 H_6, a_2 = H_4 N_1 H_5, a_3 = H_4 N_1 H_6, b_1 = C_2 N_1 H_4, b_2 = C_2 N_1 H_5, b_3 = C_2 N_1 H_6 \\
 a_4 &= H_7 C_2 H_8, a_5 = N_1 C_2 H_7, a_6 = N_1 C_2 H_8, b_4 = N_1 C_2 C_3, b_5 = C_3 C_2 H_7, b_6 = C_3 C_2 H_8 \\
 a_7 &= C_2 C_3 N_9, a_8 = C_3 N_9 H_{12}, a_9 = C_{11} N_9 H_{12}, b_7 = C_2 C_3 O_{10}, b_8 = N_9 C_3 O_{10}, b_9 = C_3 N_9 C_{11} \\
 a_{10} &= N_9 C_{11} C_{13}, a_{11} = N_9 C_{11} H_{14}, a_{12} = N_9 C_{11} H_{15}, b_{10} = H_{14} C_{11} H_{15}, b_{11} = C_{13} C_{11} H_{14}, b_{12} = C_{13} C_{11} H_{15} \\
 a_{13} &= C_{11} C_{13} O_{16}, a_{14} = O_{17} C_{13} O_{16}, b_{13} = C_{11} C_{13} O_{17}, b_{14} = C_{13} O_{17} H_{18}
 \end{aligned}$$

Figure 5.2: Internal coordinates of GGH.

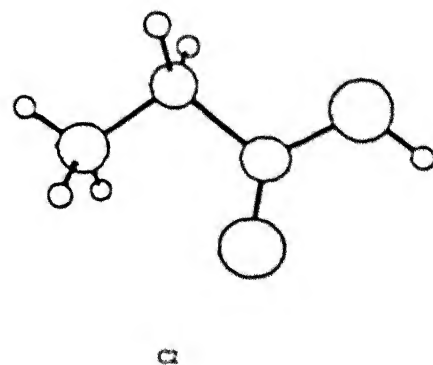
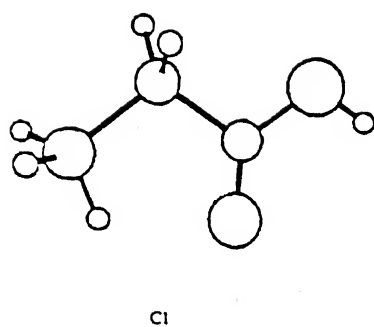


Figure 5.3: HF/6-31G\*\* optimized structures of the two conformers of GH.

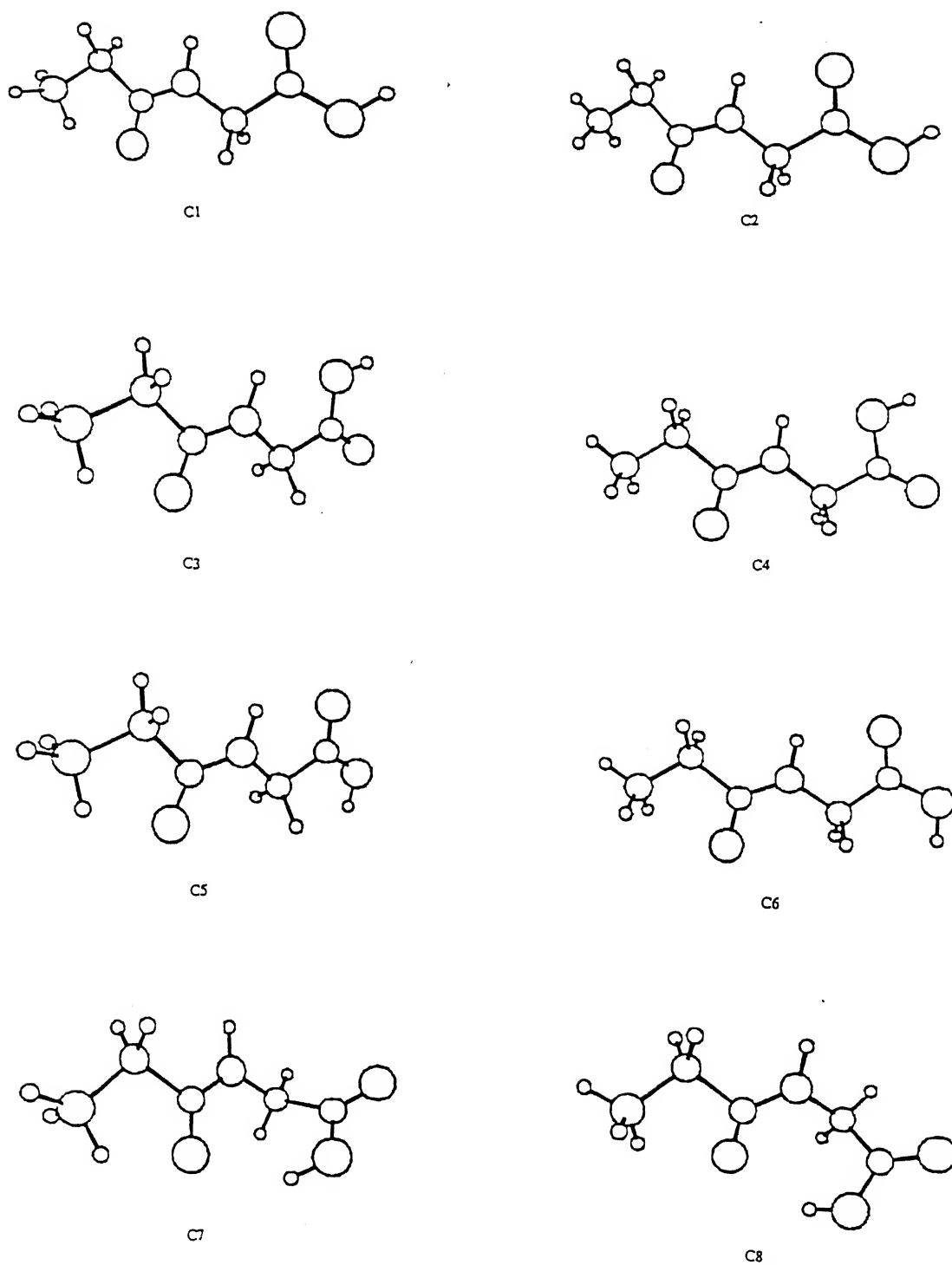


Figure 5.4: HF/6-31G\*\* optimized structures of the eight conformers of GGH.

Table 5.1: Non-redundant local coordinates\* of GH

$S_{1-10}$	$=r_{1-10}$ (all stretch)	$S_{19}$	$=2a_6-a_7-a_8(\delta_a N^+H_3)$
$S_{11}$	$=2a_1-b_1-b_2(\delta_s CO)$	$S_{20}$	$=a_7-a_8(\delta_a N^+H_3)$
$S_{12}$	$=b_1-b_2(\delta_a CO)$	$S_{21}$	$=2b_6-b_7-b_8(\rho N^+H_3)$
$S_{13}$	$=4a_3-a_4-a_5-b_4-b_5(\delta CH_2)$	$S_{22}$	$=b_7-b_8(\rho N^+H_3)$
$S_{14}$	$=a_4+a_5-b_4-b_5(\omega CH_2)$	$S_{23}$	$=a_2(\delta COH)$
$S_{15}$	$=a_4-a_5+b_4-b_5(\rho CH_2)$	$S_{24}$	$=\gamma C_1 O_5(\gamma CO)$
$S_{16}$	$=a_4-a_5-b_4+b_5(tCH_2)$	$S_{25}$	$=\tau_{12}(\tau CC)$
$S_{17}$	$=5b_3-a_3-a_4-a_5-b_4-b_5(\delta N^+CC)$	$S_{26}$	$=\tau_{14}(\tau CO)$
$S_{18}$	$=a_6+a_7+a_8-b_6-b_7-b_8(\delta_s N^+H_3)$	$S_{27}$	$=\tau_{23}(\tau CN^+)$

\* All internal coordinates are according to Figure 5.1.

Table 5.2: Non-redundant local coordinates\* of GGH

$S_{1-17}$	$=r_{1-17}$ (all stretch)	$S_{33}$	$=a_{11}+a_{12}-b_{11}-b_{12}(\omega C'H_2)$
$S_{18}$	$=a_1+a_2+a_3-b_1-b_2-b_3(\delta_s N^+H_3)$	$S_{34}$	$=a_{11}-a_{12}+b_{11}-b_{12}(\rho C'H_2)$
$S_{19}$	$=2a_1-a_2-a_3(\delta_a N^+H_3)$	$S_{35}$	$=a_{11}-a_{12}-b_{11}+b_{12}(tC'H_2)$
$S_{20}$	$=a_2-a_3(\delta_a N^+H_3)$	$S_{36}$	$=5a_{10}-b_{10}-a_{11}-a_{12}-b_{11}-b_{12}(\delta NC'C)$
$S_{21}$	$=2b_1-b_2-b_3(\rho N^+H_3)$	$S_{37}$	$=2b_{13}-a_{13}-a_{14}(\delta_s CO_{acid})$
$S_{22}$	$=b_2-b_3(\rho N^+H_3)$	$S_{38}$	$=a_{13}-a_{14}(\delta_a CO_{acid})$
$S_{23}$	$=4a_4-a_5-a_6-b_5-b_6(\delta CH_2)$	$S_{39}$	$=b_{14}(\delta COH)$
$S_{24}$	$=a_5+a_6-b_5-b_6(\omega CH_2)$	$S_{40}$	$=\gamma C_3 O_{10}(\gamma CO_{amide})$
$S_{25}$	$=a_5-a_6+b_5-b_6(\rho CH_2)$	$S_{41}$	$=\gamma N_9 H_{12}(\gamma NH)$
$S_{26}$	$=a_5-a_6-b_5+b_6(tCH_2)$	$S_{42}$	$=\gamma C_{13} O_{16}(\gamma CO_{acid})$
$S_{27}$	$=5b_4-a_4-a_5-a_6-b_5-b_6(\delta N^+CC)$	$S_{43}$	$=\tau_{12}(\tau N^+C)$
$S_{28}$	$=2a_7-b_7-b_8(\delta_s CO_{amide})$	$S_{44}$	$=\tau_{23}(\tau CC)$
$S_{29}$	$=b_7-b_8(\delta_a CO_{amide})$	$S_{45}$	$=\tau_{39}(\tau CN)$
$S_{30}$	$=2b_9-a_8-a_9(\delta_s NH)$	$S_{46}$	$=\tau_{911}(\tau NC')$
$S_{31}$	$=a_8-a_9(\delta_a NH)$	$S_{47}$	$=\tau_{1113}(\tau C'C)$
$S_{32}$	$=4b_{10}-a_{11}-a_{12}-b_{11}-b_{12}(\delta C'H_2)$	$S_{48}$	$=\tau_{1317}(\tau CO)$

\* All internal coordinates are according to Figure 5.2.



Table 5.3: Relative energies (in kJ/mol) of GH and GGH

Structure	HF/6-31G**	MP2/6-31G**
GH		
C1	15.30 (0.00)	0.03
C2	0.00 (5.07)	0.00
GGH		
C1	0.0	0.0
C2	2.2	7.1
C3	21.2	18.5
C4	23.3	25.4
C5	36.2	33.5
C6	38.2	40.2
C7	61.6	54.8
C8	60.7	53.9

The numbers in the parenthesis are the 4-21G energies.

Table 5.4: Fitted vibrational frequencies of GH ( $\text{cm}^{-1}$ )

Sym. species	6-31G** scaled	Assignments	Expt. <sup>a</sup>	SQM
1	3412	$\nu\text{OH}$	(3200)	—
2	3179	$\nu\text{N}^+\text{H}$	3182	—
3	3124	$\nu\text{N}^+\text{H}$	3152	—
4	3060	$\nu\text{N}^+\text{H}$	3058	—
5	3019	$\nu\text{CH}$	3012	3022
6	2961	$\nu\text{CH}$	2973	2961
7	1746	$\nu\text{C}=\text{O}$	1740	1750
8	1616	$\delta_a\text{N}^+\text{H}_3$	1607	1618
9	1610	$\delta_a\text{N}^+\text{H}_3$	1607	1594
10	1512	$\delta_s\text{N}^+\text{H}_3+\omega\text{CH}_2$	1512	1518
11	1489	$\delta_s\text{N}^+\text{H}_3+\omega\text{CH}_2+\nu\text{CC}+\nu\text{C}-\text{O}$	(1484)	1476
12	1427	$\delta\text{CH}_2$	1435	1434
13	1378	$\delta\text{COH}+\omega\text{CH}_2+\nu\text{C}-\text{O}$	1378	1384
14	1328	$\text{tCH}_2+\rho\text{N}^+\text{H}_3$	1320	1324
15	1252	$\nu\text{C}-\text{O}+\delta\text{COH}$	1263	1284
16	1148	$\rho\text{N}^+\text{H}_3+\omega\text{CH}_2+\nu\text{CN}^+$	1135	1153
17	1121	$\text{tCH}_2+\rho\text{N}^+\text{H}_3$	1125	1137
18	1042	$\nu\text{CN}^+$	1044	1058
19	923	$\rho\text{CH}_2+\rho\text{N}^+\text{H}_3+\gamma\text{CO}$	917	923
20	884	$\nu\text{CC}+\rho\text{N}^+\text{H}_3$	873	880
21	657	$\tau\text{CO}+\gamma\text{CO}$	657	669
22	598	$\delta_a\text{CO}+\delta\text{N}^+\text{CC}$	568	563
23	521	$\gamma\text{CO}+\tau\text{CO}+\rho\text{CH}_2$	504	453
24	498	$\delta_s\text{CO}$	(483)	—
25	297	$\delta\text{N}^+\text{CC}+\delta_s\text{CO}+\delta_a\text{CO}$	301	250
26	174	$\tau\text{CN}^++\tau\text{CC}$	(175)	—
27	34	$\tau\text{CC}+\tau\text{CN}^+$	(35)	—

a. Experimental frequencies are taken from ref. 3.

Since the fitting algorithm requires all the experimental frequencies at least for one isotopic species, the numbers in parenthesis are introduced as a good guess for GH-d<sub>0</sub> and do not have any other significance.

Table 5.5: Fitted vibrational frequencies of all the seven isotopomers of GH ( $\text{cm}^{-1}$ )

$\text{N}^+\text{H}_3\text{CH}_2\text{COOH}$		$\text{N}^+\text{H}_3\text{CH}_2^{13}\text{COOH}$		$\text{N}^+\text{H}_3\text{CD}_2\text{COOH}$		$\text{N}^+\text{D}_3\text{CH}_2\text{COOH}$		$\text{N}^+\text{D}_3^{13}\text{CH}_2\text{COOH}$		$\text{N}^+\text{D}_3\text{CH}_2^{13}\text{COOD}$		$\text{N}^+\text{D}_3\text{CH}_2^{13}\text{COOD}$	
Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
—	3412	—	3412	—	3412	—	3412	—	2184	—	2184	—	2484
3182	3179	—	3179	3182	3179	2341	2341	—	2347	—	2347	—	2347
3152	3124	—	3124	3152	3124	2263	2263	—	2306	—	2306	—	2306
3058	3060	—	3060	3058	3060	2203	2203	—	2199	—	2199	—	2199
3012	3019	—	3019	2232	2249	3015	3015	—	3007	—	3007	—	3019
2973	2961	—	2955	2166	2161	2975	2961	—	2955	—	2955	—	2961
1740	1746	1741	1745	1700	1703	1733	1733	1732	1731	1688	1687	1688	1687
1607	1616	1608	1616	1614	1614	—	1614	1166	1159	1168	1160	1168	1160
1607	1610	1608	1609	1614	1610	—	1607	—	1152	—	1153	—	1153
1512	1512	1510	1507	1520	1507	—	1503	1166	1182	1168	1186	1168	1186
—	1489	—	1481	—	1475	—	1455	—	1480	1438	1464	1438	1464
1435	1427	1431	1424	1437	1427	1429	1037	1429	1427	1406	1427	1406	1427
1378	1378	1360	1374	1370	1367	1340	1302	1340	1313	1321	1290	1321	1290
1320	1328	1316	1325	1320	1328	1278	1217	1278	1272	1271	1271	1271	1271
1263	1252	1263	1252	1246	1243	1073	1227	1073	1078	1066	1078	1066	1078
1135	1148	1133	1140	1139	1147	780	921	780	768	776	766	776	766
1125	1121	1113	1118	1119	1117	815	917	815	793	808	789	808	789
1044	1042	1027	1024	1044	1042	1008	1109	1008	1003	1007	1003	1007	1003
917	923	915	919	910	916	1043	802	1043	1042	1032	1034	1025	1034
873	884	864	873	869	881	951	837	951	956	949	956	949	956
657	657	648	657	656	653	618	632	618	598	614	589	614	589
568	598	566	595	559	596	561	592	561	552	555	550	555	550
504	521	501	521	502	514	—	463	—	419	—	417	—	417
—	498	—	496	—	497	485	487	485	470	483	468	483	468
301	297	301	296	301	296	287	295	287	275	287	274	287	274
—	174	—	172	—	174	—	166	—	148	—	148	—	148
—	34	—	34	—	34	—	33	—	27	—	27	—	27

Table 5.6: Predicted Vibrational Frequencies of GGH ( $\text{cm}^{-1}$ )

Sym. species	6-31G** scaled	Assignments	GGH expt.	GG expt. <sup>a</sup>	GGMH expt.
1	3436	$\nu\text{OH}$	—	—	—
2	3265	$\nu\text{NH}$	—	3285	—
3	3161	$\nu\text{N}^+\text{H}$	—	—	—
4	3109	$\nu\text{N}^+\text{H}$	—	—	3080
5	3017	$\nu\text{CH}$	—	3013	—
6	2977	$\nu\text{C}'\text{H}$	—	2960	2960
7	2964	$\nu\text{N}^+\text{H}+\nu\text{CH}$	—	—	—
8	2957	$\nu\text{CH}+\nu\text{N}^+\text{H}$	—	—	—
9	2938	$\nu\text{C}'\text{H}$	—	2927	—
10	1738	$\nu\text{C}=\text{O}_{\text{acid}}$	1746	—	1724
11	1676	$\nu\text{C}=\text{O}_{\text{amide}}+\nu\text{CN}$	1677	1682	1678
12	1641	$\delta_a\text{N}^-\text{H}_3$	—	1629	1648
13	1602	$\delta_a\text{N}^-\text{H}_3$	—	1611	1622
14	1593	$\delta_a\text{NH}+\nu\text{CN}+\nu\text{C}=\text{O}_{\text{amide}}+\nu\text{NC}'$	1584	1531	1535
15	1486	$\omega\text{C}'\text{H}_2+\nu\text{C}'\text{C}+\nu\text{C}-\text{O}+\omega\text{CH}_2$	1487	—	—
16	1472	$\delta_s\text{N}^+\text{H}_3+\omega\text{C}'\text{H}_2$	—	1480	1452
17	1443	$\delta\text{C}'\text{H}_2$	1434	1447	1437
18	1433	$\delta\text{CH}_2+\delta_s\text{N}^+\text{H}_3$	1434	—	1420
19	1408	$\omega\text{CH}_2+\delta\text{CH}_2$	1410	1399	1402
20	1362	$\delta\text{COH}+\omega\text{C}'\text{H}_2$	1350	—	1362
21	1329	$\text{tCH}_2+\rho\text{N}^+\text{H}_3$	1308	1315	1307
22	1266	$\delta_s\text{NH}+\nu\text{C}-\text{O}$	1265	1249	1249
23	1247	$\nu\text{C}-\text{O}+\omega\text{C}'\text{H}_2+\delta\text{COH}$	—	—	—
24	1242	$\text{tC}'\text{H}_2$	1219	1242	1219
25	1188	$\nu\text{CN}$	—	—	—
26	1155	$\rho\text{N}^+\text{H}_3+\omega\text{CH}_2+\text{tCH}_2$	1135	1158	1130
27	1126	$\text{tCH}_2+\rho\text{N}^+\text{H}_3$	1117	1100	1090
28	1050	$\nu\text{N}^+\text{C}$	1040	1046	1032
29	1002	$\rho\text{C}'\text{H}_2+\gamma\text{CO}_{\text{acid}}$	1013	1007	—
30	985	$\nu\text{CC}+\nu\text{C}'\text{C}$	—	968	980
31	925	$\rho\text{CH}_2+\gamma\text{CO}_{\text{amide}}+\rho\text{N}^+\text{H}_3$	—	918	946
32	907	$\nu\text{CC}' + \nu\text{CC}$	903	910	—
33	700	$\delta_a\text{CO}_{\text{amide}}+\delta\text{NCC}$	708	708	708
34	661	$\tau\text{CO}_{\text{acid}}+\gamma\text{CO}_{\text{acid}}+\rho\text{C}'\text{H}_2$	661	665	644
35	618	$\tau\text{CN}+\gamma\text{CO}_{\text{amide}}+\gamma\text{NH}+\rho\text{CH}_2$	—	—	—
36	594	$\delta_a\text{CO}_{\text{acid}}+\delta\text{NC}'\text{C}$	—	598	—
37	568	$\delta_s\text{CO}_{\text{acid}}+\delta_a\text{CO}_{\text{amide}}$	—	588	—
38	537	$\gamma\text{CO}_{\text{amide}}+\gamma\text{NH}$	—	535	—
39	508	$\gamma\text{CO}_{\text{acid}}+\tau\text{C}-\text{O}$	—	—	—

Table 5.6: (Continued): Predicted vibrational frequencies of GGH

40	405	$\delta N^+CC + \delta_s CO_{acid}$	—	396	—
41	331	$\delta_s CO_{amide} + \delta_s CO_{acid} + \delta_a CO_{amide}$	—	317	—
42	269	$\delta NC'C + \delta_a CO_{acid}$	—	298	—
43	196	$\tau C'C + \tau CC + \gamma NH + \tau N^+C$	—	—	—
44	179	$\tau N^+C + \tau C'C$	—	—	—
45	111	$\delta_s NH_{amide} + \delta_s CO_{amide} + tCH_2$	—	—	—
46	89	$\tau CC + \tau N^+C$	—	—	—
47	79	$\tau C'C + \tau CN$	—	—	—
48	40	$\tau NC' + \gamma NH + \tau CC$	—	—	—

a. Taken from ref. 12.

Table 5.7: Optimized cartesian coordinates of the minimum energy conformation of GH\* at 6-31G\*\* basis set

1	6	0.000000	0.000000	0.000000
2	6	0.000000	0.000000	1.516600
3	7	1.430186	0.000000	1.949957
4	8	-1.209458	0.000000	-0.475575
5	8	1.017835	0.000000	-0.606826
6	1	-1.211000	0.000000	-1.427873
7	1	-0.486890	-0.881658	1.909255
8	1	-0.486890	0.881658	1.909255
9	1	1.521335	0.000000	2.955535
10	1	1.916723	-0.805370	1.579298
11	1	1.916723	0.805370	1.579298

\* Atom numberings are according to Figure 5.1.

Table 5.8: Optimized cartesian coordinates of the minimum energy conformation of GGH\* at 6-31G\*\* basis set

1	7	0.000000	0.000000	0.000000
2	6	0.000000	0.000000	1.494700
3	6	1.477563	0.000000	1.909195
4	1	0.925435	0.336112	-0.279188
5	1	-0.105207	-0.928158	-0.380962
6	1	-0.718988	0.583323	-0.398060
7	1	-0.485599	0.902803	1.838720
8	1	-0.544079	-0.859478	1.857572
9	7	1.724873	-0.202930	3.188811
10	8	2.296971	0.202016	1.048108
11	6	3.069443	-0.181293	3.731447
12	1	0.994800	-0.372897	3.849195
13	6	2.966343	-0.442684	5.215785
14	1	3.690395	-0.941255	3.273683
15	1	3.545475	0.777382	3.566448
16	8	1.932781	-0.625710	5.772838
17	8	4.144177	-0.439886	5.788509
18	1	4.058569	-0.605608	6.720221

\* Atom numberings are according to Figure 5.2.



Table 5.9: (Continued): Non-redundant fitted force constants of GH\*

25	6	-.009	7	.009	9	-.013	10	.013	15	.071	16	-.003	20	-.019
	22	.031	24	-.009	25	.102								
26	6	.006	7	-.006	9	.002	10	-.002	15	.001	16	-.016	20	-.001
	22	-.001	24	.018	25	-.029	26	.156						
27	6	-.001	7	.001	9	-.021	10	.021	15	-.004	16	-.009	20	-.025
	22	.037	24	-.006	25	-.038	26	.000	27	.027				

\* Local symmetry coordinates are as given in Table 5.1.

Table 5.10: Non-redundant scaled force constants of GGH\*

1	1	5.023												
2	1	.195	2	4.991										
3	1	.225	2	-.008	3	4.893								
4	1	.016	2	-.001	3	.031	4	5.423						
5	1	.010	2	-.002	3	.019	4	.010	5	5.460				
6	1	.055	2	.046	3	-.002	4	-.015	5	.014	6	4.880		
7	1	.048	2	.029	3	-.007	4	.012	5	-.003	6	.032	7	4.920
8	1	-.073	2	.262	3	.071	4	-.016	5	-.012	6	.002	7	.012
	8	8.623												
9	1	.054	2	.626	3	-.148	4	.004	5	-.007	6	-.001	7	.002
	8	1.436	9	10.177										
10	1	.008	2	-.009	3	-.009	4	.003	5	.002	6	.004	7	.004
	8	.160	9	-.060	10	6.068								
11	1	-.002	2	.012	3	-.004	4	.003	5	.003	6	.002	7	.006
	8	.048	9	-.067	10	.067	11	5.896						
12	1	.002	2	-.001	3	.000	4	-.001	5	-.001	6	.000	7	.000
	8	.001	9	.021	10	.180	11	-.040	12	5.323				
13	1	.002	2	.000	3	.000	4	.000	5	.000	6	.000	7	-.001
	8	-.033	9	.025	10	.154	11	-.005	12	.039	13	4.814		
14	1	.002	2	.000	3	.000	4	.000	5	.000	6	-.001	7	-.001
	8	-.033	9	.026	10	.154	11	-.005	12	.039	13	.054	14	4.811
15	1	-.003	2	.005	3	.005	4	-.002	5	-.001	6	.000	7	.000
	8	.019	9	-.020	10	.051	11	-.049	12	.455	13	-.009	14	-.009
	15	11.351												
16	1	.000	2	.000	3	.003	4	-.003	5	-.003	6	-.001	7	-.002
	8	-.053	9	.050	10	-.005	11	.026	12	.259	13	.004	14	.004
	15	1.203	16	7.027										
17	1	.001	2	.001	3	-.001	4	.001	5	.001	6	.000	7	.000
	8	.010	9	-.006	10	-.003	11	-.002	12	-.022	13	.005	14	.005
	15	-.085	16	.132	17	6.610								





Table 5.10: (Continued): Non-redundant scaled force constants of GGH\*

30	1	.028	2	.037	3	-.015	4	.000	5	.000	6	.001	7	.000
	8	.114	9	-.033	10	.118	11	-.069	12	.003	13	-.016	14	-.016
	15	-.006	16	.049	17	-.003	18	-.006	19	-.001	20	.003	21	.005
	22	-.001	23	.001	24	.003	25	.003	26	-.003	27	.042	28	.077
	29	.062	30	.658										
31	1	-.018	2	.014	3	.008	4	.001	5	.001	6	.003	7	.005
	8	.182	9	.029	10	-.151	11	-.102	12	.029	13	-.009	14	-.009
	15	-.065	16	.039	17	-.005	18	.003	19	.000	20	-.001	21	-.004
	22	.000	23	.001	24	-.009	25	-.001	26	.004	27	-.015	28	-.004
	29	-.052	30	.011	31	.522								
32	1	.000	2	-.001	3	-.001	4	.001	5	.001	6	.001	7	.001
	8	.006	9	-.004	10	-.201	11	-.009	12	-.127	13	.078	14	.078
	15	-.022	16	.006	17	-.001	18	-.001	19	.000	20	.000	21	.001
	22	.000	23	.000	24	.000	25	.001	26	.000	27	.002	28	.004
	29	.009	30	.004	31	.017	32	.542						
33	1	.004	2	.003	3	-.001	4	-.001	5	-.001	6	-.001	7	-.002
	8	-.094	9	.052	10	.490	11	.001	12	-.171	13	-.013	14	-.013
	15	-.065	16	-.025	17	.005	18	.000	19	.000	20	.000	21	-.001
	22	.000	23	.000	24	-.001	25	.001	26	-.001	27	.001	28	.012
	29	.010	30	-.025	31	-.041	32	-.017	33	.732				
34	1	.001	2	-.002	3	.000	4	.000	5	.000	6	-.001	7	.002
	8	.002	9	.000	10	-.001	11	.001	12	.000	13	.082	14	-.082
	15	.001	16	-.001	17	.000	18	.000	19	.000	20	.000	21	.000
	22	.001	24	.001	25	-.002	26	.003	27	.002	28	-.001	29	.000
	30	.000	31	.000	32	.000	33	.000	34	.707				
35	1	.001	2	-.002	3	.000	4	.000	5	.000	6	-.002	7	.002
	8	.002	9	.000	10	.000	11	.001	13	-.037	14	.037	15	-.001
	16	.000	17	.000	18	.000	19	.000	20	.000	21	.000	22	.001
	23	.000	24	.001	25	-.004	26	.004	27	.002	28	-.001	29	.000
	30	.000	31	.000	32	.000	33	-.001	34	.114	35	.674		
36	1	.005	2	.005	3	.002	4	-.004	5	-.003	6	-.001	7	-.001
	8	.019	9	.067	10	.353	11	-.024	12	.612	13	-.035	14	-.035
	15	.074	16	.015	17	.010	18	.002	19	.000	20	-.002	21	-.005
	22	-.002	23	-.001	24	.000	25	-.001	26	-.001	27	.001	28	.001
	29	-.024	30	.032	31	.036	32	.011	33	-.042	34	.000	35	.000
	36	1.683												
37	1	.003	2	.006	3	.000	4	-.001	5	.000	6	.000	7	.00



Table 5.10: (Continued): Non-redundant scaled force constants of GGH\*

45	1	-.006	2	.014	3	.001	4	-.002	5	.001	6	.011	7	-.011
	8	-.007	9	.005	10	-.001	11	.002	12	.000	13	.002	14	-.002
	15	-.001	16	.001	17	-.001	18	.000	19	.000	20	.000	21	.002
	22	-.003	23	.002	24	-.004	25	.006	26	-.024	27	-.008	28	.007
	29	.000	30	-.001	31	.001	32	.000	33	.000	34	-.017	35	-.016
	36	.000	38	.000	39	.000	40	-.034	41	-.050	42	.002	43	.001
	44	-.029	45	.294										
46	1	.001	2	.000	3	.000	4	.000	5	.000	6	.000	7	-.001
	8	-.001	9	.000	10	.000	11	.000	12	.000	13	.016	14	-.016
	15	-.003	16	.001	18	.000	19	.000	20	.001	21	-.001	22	.001
	23	-.001	24	.000	25	-.001	26	.001	27	.000	28	.001	29	.000
	30	.000	31	.001	32	.000	33	.000	34	.014	35	.044	36	.000
	37	.000	38	.000	39	.000	40	.008	41	-.034	42	.017	43	-.001
	44	-.004	45	.004	46	.066								
47	1	.001	2	.000	3	.000	4	.000	5	.000	6	.000	7	.000
	8	.000	9	.000	10	.000	11	.000	12	.000	13	-.015	14	.015
	15	-.001	16	.000	17	-.001	18	.000	19	.000	20	.000	21	.000
	22	.001	23	-.001	24	.000	25	-.002	26	.001	27	.001	28	.000
	29	.000	30	.000	31	.000	32	.000	33	.000	34	.058	35	.014
	36	.000	37	.000	39	.000	40	.004	41	-.036	42	-.008	43	.000
	44	-.003	45	-.003	46	.047	47	.144						
48	1	.000	2	.000	3	.000	4	.000	5	.000	6	.000	7	.000
	8	.000	10	.000	12	.000	13	.007	14	-.007	15	.000	16	.000
	17	.000	19	.000	20	.000	21	.000	22	.000	23	.000	24	.000
	25	.001	26	.000	27	.000	28	.000	29	.000	30	.000	31	.000
	33	.000	34	.001	35	-.015	36	.000	37	.000	39	.000	40	.000
	41	.003	42	.012	43	.000	44	.001	45	-.001	46	.001	47	-.029
	48	.157												

\* Local symmetry coordinates are as given in Table 5.2.

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## Chapter 6

# Theoretical prediction of vibrational spectra of cysteine and serine Hydrochloride

In continuation with our earlier investigation of the vibrational spectra of hydrochlorides of amino acids glycine (GH) and glycylglycine (GGH) (chapter 5), in this chapter we address this problem, using cysteine and serine hydrochloride (CYSH and SERH).

Cysteine (CYS) owing to the presence of thiol group SH is one of the most important amino acids. It is responsible for the stabilization of secondary structures of proteins through the formation of H-bonds and more importantly disulfide bridges. Thus the CYS residue side chain,  $-\text{CH}_2\text{SH}$  was the subject of a number of spectroscopic studies for characterization of its conformers [1-23]. The theoretical modelling of thiol group in CYS is very important because the earlier force field developers have shown that an inaccurately described SH group does not tend to form H-bonds [24]. The H-bonding effect on  $\nu\text{SH}$  frequency has been studied in different proteins [1-8]. Effect of the  $\text{C}_\alpha\text{-C}_\beta\text{-S-H}$  dihedral angles on the  $\nu\text{SH}$  mode has been sought through experimental [9-11] and normal mode analyses [12,13] of some model alkanethiols. Information on rotational barriers from the low frequency torsional modes have also been reported in the literature [14-16]. The conformational assignment of  $\nu\text{CS}$  frequency with respect to  $\text{C-C}_\alpha\text{-C}_\beta\text{-S}$  dihedral angle in several thiols, [17,18] dialkyl disulfide [19,20] or alkyl sulfides [21], and the normal coordinate analyses [22,23] are found in the literature. Serine (SER) due to the presence of two hydroxyl groups readily forms H-bonds and hence is found in turns of

protein secondary structures. A study of the effect of the torsional angle  $C-C_\alpha-C_\beta-O$  on the  $\nu_{C_\beta O}$  frequency in SER was reported. [25]. There is a large number of experimental vibrational spectral study (IR and Raman) on CYS and SER zwitterions [26-31]. The most recent one being the ROA spectra of Gargaro et al. [31] based on their alanine results [32]. But a detailed theoretical vibrational analysis of both CYS and SER in their gaseous and zwitterionic forms is limited to the recent study from our laboratory based on their isolated ab initio model [25].

In this chapter our endeavour is to generate a reliable force field for CYSH and SERH. The scale factors of glycine hydrochloride from previous chapter is used to scale the ab initio force field of both the compounds at the same level of theory (HF/6-31G\*\*). The side chain residues of CYSH and SERH are scaled by using the scale factors of ethanethiol (EtSH) and ethanol (EtOH) respectively, obtained by fitting their ab initio force field to the respective experimental vibrational spectra [13,33]. A complete set of nonredundant force constants were obtained for CYSH and SERH.

## 6.1 Calculations

The ab initio force constants and frequencies of CYSH, SERH, EtSH and EtOH were calculated analytically for the optimized geometry at 6-31G\*\* level. The cartesian force constant matrices were transformed to the non-redundant local coordinate space. The nonredundant local coordinates of both EtSH and EtOH are given in Table-6.1 and Figure 6.1 and that of CYSH and SERH are given in Table-6.2 and Figure 6.2. The optimized geometries of CYSH and SERH are given in Table-6.3. The ab initio force fields of EtSH and EtOH were then fitted to their corresponding experimental spectra to obtain a non-redundant set of force constants and scale factors using the methodology described in chapter 3. The fitting is very successful for both the compounds. The scale factors of EtSH and EtOH along with glycine hydrochloride when used to scale the ab initio force field of CYSH and SERH, a very good agreement is obtained with experimental frequencies for both the molecules.



## 6.2 Results

### 6.2.1 EtSH

Of the different possible conformers, the gauche form ( $\text{H}(4)\text{-S}(2)\text{-C}(1)\text{-C}(3) \sim 60^\circ$ ) of EtSH is most stable in the ground state, as shown by Qian and Krimm, based on their ab initio (3-21G and 4-31G\*) calculations [34]. We did not do any conformational analysis further at our required level of theory (6-31G\*\*) in the present study. The fully optimized geometry of EtSH at this level generates the gauche form as the most stable one. Since the intermolecular H-bonding is less pronounced in EtSH, the isolated molecule ab initio calculation serves as a good model for the condensed phase vibrational spectra. Several experimental vibrational spectra of EtSH were found in the literature [9,13,16]. We used the condensed phase spectra [13] for the analysis. Fitted frequencies of all the fundamentals are shown in Table-6.4. Such a force field obtained from a single isotopomer frequencies might be considered as a good approximation but the reliability of this force field should be judged by its ability to predict the vibrational frequencies of CYSH. The fitted force field retains the ab initio PEDs in all the frequencies. The  $2571\text{ cm}^{-1}$  band is assigned to  $\nu\text{SH}$ , the  $\nu\text{CC}$  mode appears at  $1052\text{ cm}^{-1}$  and  $970\text{ cm}^{-1}$  and  $\nu\text{CS}$  is assigned to the band at  $657\text{ cm}^{-1}$ . These are in good agreement with the earlier assignments of EtSH and Propane thiol (PrSH) [34].

### 6.2.2 EtOH

In EtOH the most staggered conformation is the most stable one at 6-31G\*\* level of calculation [35]. The trans-gauche rotational barrier is known to be  $4.89\text{ kJ/mol}$  [36]. The earlier microwave study also indicates the trans form as the more stable one over the gauche form [37]. So we calculated the ab initio force field for the fully optimized staggered(trans) conformer of EtOH only at the required 6-31G\*\* level of theory. In condensed phase there exists intermolecular H-bonding in EtOH and the corresponding vibrational spectra will be different from the isolated molecular spectra. However the isolated molecule-ab initio model can serve as a reasonable approximation to the condensed phase vibrational spectra

when *fitted* to the *experimental numbers*. Several experimental vibrational spectra of EtOH in liquid, crystal and/or vapour phase are available in the literature [33,38,39]. For the present study we used the liquid and crystal frequencies of EtOH and EtOD of Mikawa et al. [33]. The fitted numbers are in good agreement for all the fundamentals, except the  $\nu\text{OH}$ , which is highly overestimated in the isolated model calculation compared to the condensed phase experimentally observed frequency. So this frequency is not included in the error estimation. The average error is  $4.0\text{ cm}^{-1}$  for the observed fundamentals. The normal modes obtained after fitting the experimental frequencies to the calculated ones agree well with the earlier reported assignments with few exceptions. The  $\delta\text{COH}$  appears as a mixed mode in the ab initio PED with  $\omega\text{CH}_2$  at  $1430\text{ cm}^{-1}$ , while the earlier experimental assignment was at  $1328\text{ cm}^{-1}$ , which we assign to  $\nu\text{CH}_2$  mode. The assignment of the corresponding  $\delta\text{COD}$  ( $954\text{ cm}^{-1}$ ) matches well with the earlier assignment. We assigned the  $\delta\text{CCO}(\gamma\text{OH})$  mode at  $439\text{ cm}^{-1}$ , which was earlier assigned at  $657\text{ cm}^{-1}$  in IR and  $660\text{ cm}^{-1}$  in polarized Raman [33]. The usefulness of the calculated force field could be tested by its ability to predict the vibrational spectra of the side chain residue of SERH successfully.

### 6.2.3 Vibrational Frequencies of CYSH

The predicted frequencies of CYSH are given in Table-6.5 along with their PEDs. The prediction is in good agreement with the experimental frequencies producing an average error of  $11.9\text{ cm}^{-1}$  for CYSH spectra. Since glycine does not have any chiral carbon atom, the scale factors for the methylene group is difficult to transfer to the higher amino acids. But these bending modes generally appear around  $1000\text{-}1400\text{ cm}^{-1}$  and a simple Durig's scaling produces reasonable agreement with the observed bands in this region. The side chain  $-\text{CH}_2\text{SH}$  residue is successfully represented by using the scale factors from EtSH. There is no detailed assignment of IR/Raman spectra of CYSH in the literature except the earlier report from our laboratory [25]. We re-recorded the spectra of CYSH (commercial sample of L-cysteine hydrochloride from S. D. Fine Chemicals, India) as a mull in Nujol in the spectral range of  $600\text{-}4000\text{ cm}^{-1}$ . The CYS-OMe spectra [25] and the L-CYS zwitterionic spectra [30] are also included in the Table-6.5 for a comparison.

The observed band at  $3377\text{ cm}^{-1}$  in CYSH is assigned to  $\nu\text{OH}$  and is calculated at  $3407\text{ cm}^{-1}$ . All the three  $\nu\text{N}^+\text{H}$  bands are predicted above the  $\nu\text{CH}$  bands at  $3166$ ,  $3115$  and  $3019\text{ cm}^{-1}$ . These bands are not observed in our spectra of CYSH and CYS-OMe. However in L-CYS zwitterion, these bands appear at  $3167$  and  $3055\text{ cm}^{-1}$ . The  $\nu\text{SH}$  band is predicted at  $2590\text{ cm}^{-1}$  and is observed at  $2567\text{ cm}^{-1}$  in the CYSH spectra. This assignment is in accordance with the observed bands at  $2571\text{ cm}^{-1}$  in EtSH,  $2564\text{ cm}^{-1}$  in PrSH and around  $2590\text{ cm}^{-1}$  in the model protein for cysteine residue [34] and also  $2582\text{ cm}^{-1}$  in zwitterion. The  $\nu\text{C}_\beta\text{S}$  is predicted at  $680\text{ cm}^{-1}$  and is also comparable to EtSH ( $660\text{ cm}^{-1}$ ) and PtSH ( $655\text{ cm}^{-1}$ ) but appear at  $696\text{ cm}^{-1}$  in the zwitterion. This band is not observed in our CYSH and CYS-OMe spectra. The  $\nu\text{C=O}$  band is slightly overestimated in the predicted spectra ( $1776\text{ cm}^{-1}$ ) and this mode is assigned to the observed band at  $1743\text{ cm}^{-1}$  in CYSH and  $1735\text{ cm}^{-1}$  in CYS-OMe. This band is observed at  $1750\text{ cm}^{-1}$  in glycine hydrochloride. Both the  $\delta_\alpha\text{N}^+\text{H}_3$  appear very close in our predicted spectra followed by  $\delta_\beta\text{N}^+\text{H}_3$  band. Both the  $\delta_\alpha\text{N}^+\text{H}_3$  are predicted at  $1634$  and  $1614\text{ cm}^{-1}$  and are assigned to the observed bands at  $1633$  and  $1613\text{ cm}^{-1}$  in our CYSH spectra and the lower one corresponds to the  $1593\text{ cm}^{-1}$  CYS-OMe spectra. These two bands are observed at  $1616\text{ cm}^{-1}$  in the zwitterion. The  $\delta_\beta\text{N}^+\text{H}_3$  band is predicted at  $1481\text{ cm}^{-1}$  and is assigned to the observed band at  $1490\text{ cm}^{-1}$  in CYSH. In our predicted spectra the  $\nu\text{CC}+\nu\text{CO}$  mode appear above  $\delta\text{CH}_2$  in accordance with glycine hydrochloride. But in zwitterion they appear in the reverse order. The predicted bands at  $1444$  and  $1410\text{ cm}^{-1}$  are assigned to  $\nu\text{CC}+\nu\text{CO}$  and  $\delta\text{C}_\beta\text{H}_2$  and are observed at  $1428$  and  $1399\text{ cm}^{-1}$  in CYSH and  $1437$  and  $1408\text{ cm}^{-1}$  in CYS-OMe and  $1427$  and  $1400\text{ cm}^{-1}$  in the zwitterion. The  $\delta\text{COH}$  mode is predicted at  $1348\text{ cm}^{-1}$ , and is observed at  $1348\text{ cm}^{-1}$  in CYSH spectra and obviously absent in the CYS-OMe and zwitterionic spectra. Both the  $\omega\text{C}_\beta\text{H}_2$  and  $\text{tC}_\beta\text{H}_2$  modes are attributed to the predicted bands at  $1292$  and  $1196\text{ cm}^{-1}$  and are observed at  $1309$ ,  $1203\text{ cm}^{-1}$  in CYSH and  $1313$ ,  $1205\text{ cm}^{-1}$  in CYS-OMe spectra. These bands appear at  $1300$  and  $1201\text{ cm}^{-1}$  in CYS zwitterion. Both the  $\rho\text{N}^+\text{H}_3$  modes are predicted at  $1161$  and  $1102\text{ cm}^{-1}$  as expected and only one of them appear in our observed spectra. The  $1069\text{ cm}^{-1}$  predicted band is assigned to  $\nu\text{C}_\alpha\text{N}^+$  and is attributed to the observed band at  $1059\text{ cm}^{-1}$  in CYSH and  $1068\text{ cm}^{-1}$  in zwitterion. The observed band at  $736\text{ cm}^{-1}$  in both the spectra is assigned to

$\gamma\text{CO}+\nu\text{CC}+\nu\text{CN}^+$  mode and is predicted at  $732\text{ cm}^{-1}$ . The lower frequency modes below  $400\text{ cm}^{-1}$  are not available and hence our predicted numbers cannot be compared.

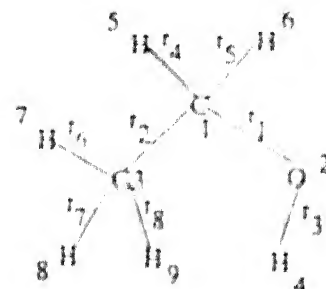
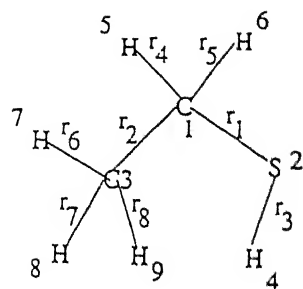
#### 6.2.4 Vibrational Frequencies of SERH

The predicted frequencies of SERH along with the PED is given in Table-6.6. Same strategy of transferring the scale factors of glycine hydrochloride and EtOH, as in CYSH was used. There is no report on the IR or Raman spectra of SERH in the literature except that reported from our laboratory earlier [25]. We have used the same reported spectra for SERH and SER-OMe for the present study. Since only few bands are observed in these two spectra it is difficult to judge the accuracy of our prediction. As a result, vibrational frequencies from both L-serine and D,L-serine [29] are included in Table-6.6. The average error is difficult to estimate in such cases. In case of SERH and SER-OMe spectra the average is quite high ( $13.1$  and  $12.2\text{ cm}^{-1}$ ) for 11 and 17 observed frequencies respectively out of the expected 39 fundamentals. The  $\nu\text{OH}_{(\text{alc})}$  is predicted above  $\nu\text{OH}_{(\text{acid})}$  as expected. The  $\nu\text{C=O}$  band is predicted at  $1744\text{ cm}^{-1}$  and matches very well with the observed numbers at  $1734$  in SERH and  $1735$  in SER-OMe spectra. Both the  $\delta_s\text{N}^+\text{H}_3$  bands appear at the same region in our predicted spectra, as in case of CYSH. Both the  $\delta_s\text{C}_\beta\text{H}_2$  and  $\delta_s\text{N}^+\text{H}_3$  modes are predicted very close to each other, though  $\delta_s\text{N}^+\text{H}_3$  appear below  $\delta_s\text{C}_\beta\text{H}_2$ . Many of the other modes  $\rho\text{CC}_\beta\text{H}$  ( $1365$ ),  $\delta\text{COH}$  ( $1340$ ),  $\nu\text{CO} + \delta\text{COH}$  ( $1249$ ),  $\rho\text{N}^+\text{H}_3$  ( $1174, 1144$ ),  $\nu\text{CN}^+$  ( $1094$ ) and  $\gamma\text{CO}$  ( $728$ ) in our predicted SERH spectra appear very similar to their corresponding observed frequencies. The  $\text{tCH}_2$  ( $1297$ ) appear above the  $\omega\text{CH}_2$  ( $1225$ ) in the predicted SERH spectra, reverse to that of CYSH. The  $\delta\text{C}_\alpha\text{OH}$  mode is expected to appear at much higher frequency compared to the  $\delta\text{C}_\beta\text{SH}$  mode in CYSH. As a result the  $1437\text{ cm}^{-1}$  band in SERH correspond to  $\delta\text{C}_\alpha\text{OH}$ , whereas the  $\delta\text{C}_\beta\text{SH}$  band in CYSH appear at  $991\text{ cm}^{-1}$  in our prediction. A comparison of the amino acid backbone and side chain frequencies of all related molecules used in the present study appear in Tables-6.7 and 6.8.

The predicted non redundant force constants of both CYSH and SERH are given in Table-6.9 and 6.10 respectively.

## 6.3 Conclusions

The theoretical prediction of amino acid hydrochloride vibrational spectra based on isolated *ab initio* calculation is found to be very successful. The choice of right basis set is considered to be an important factor for mimicking the experimental spectra through isolated molecule *ab initio* model. The scale factors of smallest amino acid, glycine is found to be very useful in predicting the higher chiral amino acids. The earlier prediction of glycylglycine hydrochloride and the present study, led us to infer that this nonredundant set of scale factors of glycine hydrochloride could be used to predict successfully the vibrational spectra of other amino acids and structurally related dipeptides in acidic pH. However further study of other amino acids is needed to verify this conclusion. This further implies that the structurally related small organic compounds can be used to mimic the amino acid side chain residues.



- $a = C(1)-O(2)/S(2)-H(4)$ ,  $a_1 = H(5)-C(1)-H(6)$ ,  $a_2 = C(3)-C(1)-H(5)$   
 $a_3 = C(3)-C(1)-H(6)$ ,  $b_1 = C(3)-C(1)-O(2)/S(2)$ ,  $b_2 = O(2)/S(2)-C(1)-H(5)$   
 $b_3 = O(2)/S(2)-C(1)-H(6)$ ,  $a_4 = H(8)-C(3)-H(9)$ ,  $a_5 = H(7)-C(3)-H(8)$   
 $a_6 = H(7)-C(3)-H(9)$ ,  $b_4 = C(1)-C(3)-H(7)$ ,  $b_5 = C(1)-C(3)-H(8)$ ,  $b_6 = C(1)-C(3)-H(9)$

Figure 6.1: Internal coordinates of EtSH and EtOH.

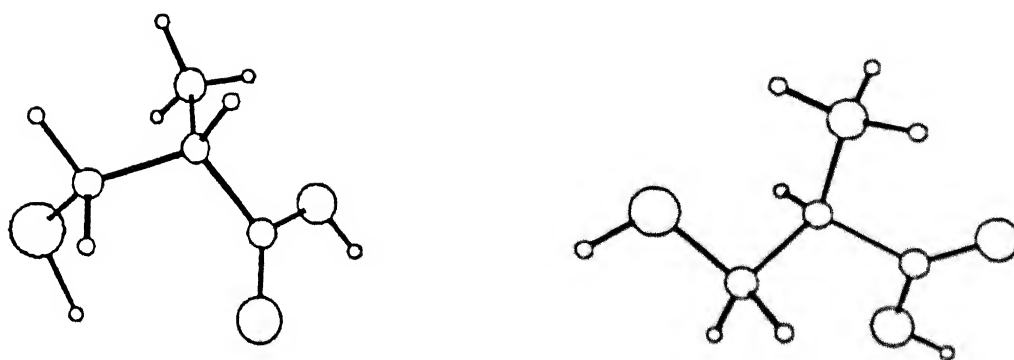


Figure 6.3: Optimized structure of a) CYSH and b) SERH at HF/6-31G\*\* level.

Table 6.1: Local symmetry coordinates of EtSH and EtOH \*

$S_{1-8}=$	$r_{1-8}(\text{all stretch})$	$S_{15}=$	$a_4+a_5+a_6-b_4-b_5-b_6 (\delta_s \text{CH}_3)$
$S_9=$	$4a_1-a_2-a_3-b_2-b_3 (\delta \text{CH}_2)$	$S_{16}=$	$2a_4-a_5-a_6 (\delta_a \text{CH}_3)$
$S_{10}=$	$a_2+a_3-b_2-b_3 (\omega \text{CH}_2)$	$S_{17}=$	$a_5-a_6 (\delta_a \text{CH}_3)$
$S_{11}=$	$a_2-a_3+b_2-b_3 (\rho \text{CH}_2)$	$S_{18}=$	$2b_4-b_5-b_6 (\rho \text{CH}_3)$
$S_{12}=$	$a_2-a_3-b_2+b_3 (\text{tCH}_2)$	$S_{19}=$	$b_5-b_6 (\rho \text{CH}_3)$
$S_{13}=$	$5b_1-a_1-a_2-a_3-b_2-b_3 (\delta \text{CCS}/\delta \text{CCO})$	$S_{20}=$	$\tau_{1-2} (\tau \text{CS}/\tau \text{CO})$
$S_{14}=$	$a (\delta \text{CSH}/\delta \text{COH})$	$S_{21}=$	$\tau_{1-3} (\tau \text{CC})$

\* Internal coordinate numberings are according to Figure 6.1.

Table 6.2: Local symmetry coordinates of CYSH and SERH \*

$S_{1-14}=$	$r_{1-14}(\text{all stretch})$	$S_{27}=$	$b_7-b_8 (\rho \text{COO})$
$S_{15}=$	$a_1+a_2+a_3-b_1-b_2-b_3 (\delta \text{N}^+ \text{C}_\alpha \text{C})$	$S_{28}=$	$a_8 (\delta \text{COH})$
$S_{16}=$	$2a_1-a_2-a_3 (\delta \text{C}_\beta \text{C}_\alpha \text{C})$	$S_{29}=$	$4a_9-a_{10}-a_{11}-b_{10}-b_{11} (\delta \text{C}_\beta \text{H}_2)$
$S_{17}=$	$a_2-a_3 (\rho \text{C}_\beta \text{C}_\alpha \text{C})$	$S_{30}=$	$a_{10}+a_{11}-b_{10}-b_{11} (\omega \text{C}_\beta \text{H}_2)$
$S_{18}=$	$2b_1-b_2-b_3 (\delta \text{C}_\beta \text{C}_\alpha \text{H})$	$S_{31}=$	$a_{10}-a_{11}+b_{10}-b_{11} (\rho \text{C}_\beta \text{H}_2)$
$S_{19}=$	$b_2-b_3 (\rho \text{C}_\beta \text{C}_\alpha \text{H})$	$S_{32}=$	$a_{10}-a_{11}-b_{10}+b_{11} (\text{tC}_\beta \text{H}_2)$
$S_{20}=$	$a (\delta \text{C}_\beta \text{SH}/\delta \text{C}_\beta \text{OH})$	$S_{33}=$	$5b_9-a_9-a_{10}-a_{11}-b_{10}-b_{11} (\delta \text{C}_\alpha \text{C}_\beta \text{S}/\delta \text{C}_\alpha \text{C}_\beta \text{O})$
$S_{21}=$	$a_4+a_5+a_6-b_4-b_5-b_6 (\delta_s \text{N}^+ \text{H}_3)$	$S_{34}=$	$\gamma_{710}/\gamma_{726} (\gamma \text{C}=\text{O})$
$S_{22}=$	$2a_4-a_5-a_6 (\delta_a \text{N}^+ \text{H}_3)$	$S_{35}=$	$\tau_{15}/\tau_{48} (\tau \text{C}_\beta \text{S}/\tau \text{C}_\beta \text{O})$
$S_{23}=$	$a_5-a_6 (\delta_a \text{N}^+ \text{H}_3)$	$S_{36}=$	$\tau_{26}/\tau_{13} (\tau \text{C}_\alpha \text{N}^+)$
$S_{24}=$	$2b_4-b_5-b_6 (\rho \text{N}^+ \text{H}_3)$	$S_{37}=$	$\tau_{12}/\tau_{14} (\tau \text{C}_\alpha \text{C}_\beta)$
$S_{25}=$	$b_5-b_6 (\rho \text{N}^+ \text{H}_3)$	$S_{38}=$	$\tau_{27}/\tau_{12} (\tau \text{C}_\alpha \text{C})$
$S_{26}=$	$2a_7-b_7-b_8 (\delta \text{COO})$	$S_{39}=$	$\tau_{711}/\tau_{27} (\tau \text{CO})$

\* Internal coordinate numberings are according to Figure 6.2.



Table 6.3: Optimized geometrical parameters of CYSH and SERH (6-31G\*\*)

param	CYSH	SERH	param	CYSH	SERH	param	CYSH	SERH
r <sub>1</sub>	1.530	1.531	a <sub>3</sub>	112.8	113.6	b <sub>4</sub>	114.0	104.6
r <sub>2</sub>	1.083	1.088	b <sub>1</sub>	110.2	109.4	b <sub>10</sub>	106.6	111.6
r <sub>3</sub>	1.079	1.083	b <sub>2</sub>	106.4	107.3	b <sub>11</sub>	110.5	112.9
r <sub>4</sub>	1.818	1.395	b <sub>3</sub>	107.0	110.7	$\tau_{2159}/\tau_{14815}$	79.7	173.5
r <sub>5</sub>	1.505	1.497	a <sub>4</sub>	107.7	109.4	$\tau_{6213}/\tau_{31412}$	-65.3	-72.2
r <sub>6</sub>	1.527	1.518	a <sub>5</sub>	108.2	106.4	$\tau_{6215}/\tau_{3148}$	54.2	48.0
r <sub>7</sub>	1.085	1.082	a <sub>6</sub>	108.6	110.0	$\tau_{7213}/\tau_{21412}$	171.6	46.7
r <sub>8</sub>	1.326	0.946	b <sub>4</sub>	111.3	110.4	$\tau_{7215}/\tau_{2148}$	-68.8	166.1
r <sub>9</sub>	1.176	1.185	b <sub>5</sub>	109.5	111.9	$\tau_{12612}/\tau_{4139}$	-169.7	81.1
r <sub>10</sub>	1.321	1.304	b <sub>6</sub>	111.5	108.8	$\tau_{82612}/\tau_{5139}$	70.6	-160.7
r <sub>11</sub>	1.011	1.012	a <sub>7</sub>	111.5	111.5	$\tau_{72612}/\tau_{2139}$	-44.8	-41.9
r <sub>12</sub>	1.015	1.013	a <sub>8</sub>	111.0	111.3	$\tau_{12710}/\tau_{4126}$	-31.0	-114.1
r <sub>13</sub>	1.010	1.009	b <sub>7</sub>	122.4	121.5	$\tau_{62710}/\tau_{3126}$	-154.7	5.6
r <sub>14</sub>	0.953	0.952	b <sub>8</sub>	126.0	127.0	$\tau_{82710}/\tau_{5126}$	90.3	122.3
a	97.8	112.2	a <sub>9</sub>	107.5	108.7	$\tau_{271115}/\tau_{12714}$	176.8	-179.4
a <sub>1</sub>	109.4	107.0	a <sub>10</sub>	109.8	110.6	$\tau_{1071115}/\tau_{62714}$	-1.2	-0.4
a <sub>2</sub>	110.7	108.5	a <sub>11</sub>	108.1	108.3			

\* All internal coordinates are according to Figure 6.2.

Table 6.4: Fitted frequencies of EtSH and EtOH

no.	EtSH			EtOH			EtOD		
	expt <sup>a</sup>		PED	expt <sup>b</sup>		PED	expt <sup>b</sup>		PED
	calc			calc			calc		
1	2988	2988	$\nu C(H_3)+\nu C(H_2)$	3336	3511	$\nu OH$	2557		$\nu OD$
2	2967	2967	$\nu C(H_2)+\nu C(H_3)$	2975	2975	$\nu C(H_3)$	2975		$\nu C(H_3)$
3	2932	2932	$\nu C(H_2)$	2940	2940	$\nu C(H_3)$	2940		$\nu C(H_3)$
4	2902	2902	$\nu C(H_2)$	2920	2920	$\nu C(H_2)$	2920		$\nu C(H_2)$
5	2875	2875	$\nu C(H_3)$	2890	2890	$\nu C(H_3)$	2890		$\nu C(H_3)$
6	2571	2571	$\nu SH$	2877	2877	$\nu C(H_2)$	2877		$\nu C(H_2)$
7	1460	1460	$\delta_a CH_3$	1498	1494	$\delta CH_2$	1490	1490	$\delta CH_2+\delta_a CH_3$
8	1450	1450	$\delta_a CH_3$	1480	1478	$\delta_a CH_3$	1474	1475	$\delta_a CH_3+\delta CH_2$
9	1434	1434	$\delta CH_2$	1450	1449	$\delta_a CH_3+\rho CH_3$	1447	1449	$\delta_a CH_3+\rho CH_3$
10	1376	1376	$\delta_s CH_3$	1430	1446	$\delta COH+\omega CH_2+\delta CH_2+\delta_a CH_3$	1404	1401	$\delta_s CH_3+\omega CH_2+\nu CC$
11	1273	1273	$\omega CH_2$	1381	1385	$\delta_s CH_3$	1365	1357	$\omega CH_2+\delta_s CH_3$
12	1251	1251	$t CH_2+\rho CH_3$	1328	1318	$t CH_2+\rho CH_3$	1309	1318	$t CH_2+\rho CH_3$
13	1091	1091	$\rho CH_3+\delta CSH+t CH_2+\rho CH_2$	1273	1277	$\omega CH_2+\delta COH$	1170	1170	$\rho CH_3+t \delta COD+\delta CCO+\nu CC$
14	1052	1052	$\nu CC+t \rho CH_3+t CH_2$	1149	1153	$\rho CH_2+\rho CH_3+t CH_2$	1158	1153	$\rho CH_2+\rho CH_3+t CH_2$
15	970	970	$\nu CC+\rho CH_3$	1089	1091	$\rho CH_3$	1055	1054	$\nu CO+\nu CC$
16	869	869	$\delta CSH+t CH_2+\rho CH_3$	1050	1051	$\nu CC+\nu CO$	954	946	$\delta COD+\rho CH_3+\omega CH_2$
17	737	737	$\rho CH_2+t \rho CH_3+t \delta CSH$	880	887	$\nu CO+\nu CC+\rho CH_3$	877	870	$\nu CO+\nu CC+\rho CH_3$
18	657	657	$\nu CS$	802	799	$\rho CH_2+\rho CH_3+t CH_2$	797	799	$\rho CH_2+\rho CH_3+t CH_2$
19	319	319	$\delta CCS$	433	439	$\delta CCO+\rho CH_3$	435	429	$\delta CCO+\rho CH_3$
20	247	247	$\tau CC$	264	264	$\tau CO+\tau CC$		236	$\tau CC$
21	191	191	$\tau CS$	200	219	$\tau CC+\tau CO$		183	$\tau CO+\tau CC$

a. ref. [14] b. ref. [34]

Table 6.5: Predicted frequencies and PED of CYSH

no.	calc	PED	expt		
			CYSH <sup>a</sup>	CYS-OMe <sup>a</sup>	CYS-zwitt. <sup>b</sup>
1	3407	$\nu\text{OH}$	3377	—	—
2	3166	$\nu\text{N}^+\text{H}$	—	—	3167
3	3115	$\nu\text{N}^+\text{H}$	—	—	—
4	3019	$\nu\text{N}^+\text{H}$	—	—	3055
5	3003	$\nu\text{C}_\beta\text{H}$	—	3000	2998
6	2950	$\nu\text{C}_\beta\text{H}$	2943	2953	2960
7	2934	$\nu\text{C}_\alpha\text{H}$	2943	—	2918
8	2590	$\nu\text{SH}$	2567	—	2582
9	1776	$\nu\text{C}=\text{O}$	1743	1735	—
10	1634	$\delta_\alpha\text{N}^+\text{H}_3$	1633	—	1616
11	1614	$\delta_\alpha\text{N}^+\text{H}_3$	1613	1593	1616
12	1481	$\delta_s\text{N}^+\text{H}_3$	1490	—	—
13	1444	$\nu\text{CC}+\nu\text{CO}+\rho\text{C}_\beta\text{C}_\alpha\text{H}$	1428	1437	1427
14	1410	$\delta\text{C}_\beta\text{H}_2$	1399	1408	1400
15	1357	$\rho\text{C}_\beta\text{C}_\alpha\text{H}+\delta\text{C}_\beta\text{C}_\alpha\text{H}$	1371	1377	1351
16	1348	$\delta\text{COH}+\delta\text{C}_\beta\text{C}_\alpha\text{H}+\rho\text{N}^+\text{H}_3$	1348	—	—
17	1292	$\omega\text{C}_\beta\text{H}_2$	1309	1313	1300
18	1221	$\nu\text{CO}+\delta\text{COH}+\rho\text{C}_\beta\text{C}_\alpha\text{H}$	1222	—	—
19	1196	$\text{tC}_\beta\text{H}_2+\delta\text{C}_\beta\text{C}_\alpha\text{H}$	1203	1205	1201
20	1161	$\rho\text{N}^+\text{H}_3+\rho\text{C}_\beta\text{C}_\alpha\text{H}$	1141	1176	—
21	1102	$\rho\text{N}^+\text{H}_3+\text{tC}_\beta\text{H}_2+\delta\text{C}_\beta\text{C}_\alpha\text{H}$	1141	1176	—
22	1069	$\nu\text{C}_\alpha\text{N}^++\delta\text{C}_\beta\text{SH}$	1059	—	1068
23	991	$\delta\text{C}_\beta\text{SH}+\nu\text{C}_\alpha\text{C}_\beta+\rho\text{N}^+\text{H}_3+\rho\text{C}_\beta\text{H}_2$	988	1009	1004
24	943	$\nu\text{C}_\alpha\text{N}^++\nu\text{C}_\alpha\text{C}_\beta+\delta\text{C}_\beta\text{SH}+\nu\text{C}_\alpha\text{C}$	931	942	943
25	852	$\delta\text{N}^+\text{C}_\alpha\text{C}+\gamma\text{CO}+\nu\text{C}_\alpha\text{C}$	863	882	870
26	779	$\rho\text{C}_\beta\text{H}_2+\delta\text{C}_\beta\text{SH}$	777	781	773
27	732	$\gamma\text{CO}+\nu\text{C}_\alpha\text{C}+\nu\text{C}_\alpha\text{N}^+$	736	736	—
28	680	$\nu\text{C}_\beta\text{S}$	—	—	696
29	621	$\tau\text{CO}+\nu\text{C}_\beta\text{S}$	644	637	642
30	549	$\delta\text{COO}+\delta\text{C}_\beta\text{C}_\alpha\text{C}$	—	—	—
31	513	$\rho\text{COO}$	524	—	—
32	444	$\delta\text{N}^+\text{C}_\alpha\text{C}+\gamma\text{CO}+\delta\text{C}_\alpha\text{C}_\beta\text{S}$	458	—	—
33	327	$\rho\text{C}_\beta\text{C}_\alpha\text{C}+\delta\text{C}_\beta\text{C}_\alpha\text{C}+\tau\text{C}_\beta\text{S}$	—	—	—
34	315	$\tau\text{C}_\beta\text{S}$	—	—	—
35	270	$\rho\text{C}_\beta\text{C}_\alpha\text{C}+\tau\text{C}_\alpha\text{N}^++\delta\text{COO}+\delta\text{C}_\beta\text{C}_\alpha\text{C}+\tau\text{C}_\beta\text{S}$	—	—	—
36	242	$\tau\text{C}_\alpha\text{N}^++\tau\text{C}_\beta\text{S}$	—	—	—
37	193	$\delta\text{C}_\alpha\text{C}_\beta\text{S}+\delta\text{N}^-\text{C}_\alpha\text{C}+\tau\text{CC}_\beta$	—	—	—
38	94	$\tau\text{C}_\alpha\text{C}_\beta$	—	—	—
39	59	$\tau\text{C}_\alpha\text{C}$	—	—	—

a. Ref. [26] and present study

b. Ref. [31]

Table 6.6: Predicted frequencies and PED of SERH

no.	calc	PED	expt		
			SERH <sup>a</sup>	SER-OMe <sup>a</sup>	SER-zwitt. <sup>b</sup>
1	3490	$\nu\text{OH}_{alc}$	—	—	—
2	3412	$\nu\text{OH}_{acid}$	3385	—	—
3	3155	$\nu\text{N}^+\text{H}$	—	—	—
4	3132	$\nu\text{N}^+\text{H}$	—	—	—
5	3045	$\nu\text{N}^+\text{H}$	—	—	—
6	3000	$\nu\text{C}_\beta\text{H}_2$	—	—	—
7	2970	$\nu\text{C}_\alpha\text{H}$	—	2956	2975
8	2937	$\nu\text{C}_\beta\text{H}_2$	—	—	2945
9	1744	$\nu\text{C}=\text{O}$	1734	1735	—
10	1628	$\delta_n\text{N}^+\text{H}_3$	—	—	(1637)
11	1612	$\delta_n\text{N}^+\text{H}_3$	—	1596	(1626)
12	1484	$\delta\text{C}_\beta\text{H}_2$	—	—	—
13	1481	$\delta_s\text{N}^+\text{H}_3$	—	—	—
14	1471	$\delta_s\text{N}^+\text{H}_3+\nu\text{C}-\text{O}+l\text{C}_\alpha\text{C}$	—	1450	1450
15	1437	$\delta\text{C}_\beta\text{OH}+\omega\text{C}_\beta\text{H}_2+\nu\text{C}_\alpha\text{C}_\beta$	1408	—	1435
16	1365	$\rho\text{C}_\beta\text{C}_\alpha\text{H}+\delta\text{C}_\beta\text{C}_\alpha\text{H}+\delta\text{COH}$	—	1378	1364
17	1340	$\delta\text{COH}+\delta\text{C}_\beta\text{C}_\alpha\text{H}+\delta\text{C}_\beta\text{OH}$	1344	1346	—
18	1297	$t\text{C}_\beta\text{H}_2$	—	1309	1312
19	1249	$\nu\text{C}-\text{O}+\delta\text{COH}$	1242	—	1248
20	1225	$\omega\text{C}_\beta\text{H}_2+\delta\text{C}_\beta\text{OH}$	—	1227	—
21	1174	$\delta\text{C}_\beta\text{C}_\alpha\text{H}+\rho\text{N}^+\text{H}_3+t\text{C}_\beta\text{H}_2+\rho\text{C}_\beta\text{H}_2$	—	1177	1180
22	1144	$\rho\text{N}^+\text{H}_3+\rho\text{C}_\beta\text{C}_\alpha\text{H}+\nu\text{C}_\alpha\text{N}^+$	1132	1131	1162
23	1094	$\nu\text{C}_\alpha\text{N}^++\nu\text{C}_\alpha\text{C}_\beta$	1077	1064	1095
24	1030	$\nu\text{C}_\beta\text{O}$	1025	1044	1030
25	980	$\rho\text{C}_\beta\text{H}_2+\nu\text{C}_\alpha\text{C}_\beta+\rho\text{N}^+\text{H}_3$	970	—	983
26	947	$\rho\text{C}_\beta\text{H}_2+\nu\text{CC}_\alpha$	—	945	—
27	852	$\nu\text{C}_\alpha\text{N}^++\rho\text{C}_\beta\text{H}_2+\nu\text{C}_\alpha\text{C}_\beta$	829	857	849
28	728	$\gamma\text{CO}+\tau\text{CO}$	—	—	—
29	620	$\rho\text{COO}+\tau\text{CO}$	—	635	(619)
30	583	$\tau\text{CO}+\delta\text{C}_\alpha\text{C}_\beta\text{O}+\rho\text{COO}+\gamma\text{CO}$	—	562	566
31	539	$\delta\text{COO}+\delta\text{N}^-\text{C}_\alpha\text{C}$	538	514	525
32	425	$\delta\text{C}_\alpha\text{C}_\beta\text{O}+\delta\text{COO}+\nu\text{CC}_\alpha$	—	—	—
33	340	$\delta\text{N}^+\text{C}_\alpha\text{C}+\delta\text{CC}_\alpha\text{C}_\beta+\delta\text{C}_\alpha\text{C}_\beta\text{O}$	—	—	—
34	300	$\delta\text{CC}_\alpha\text{C}_\beta+\delta\text{COO}+\delta\text{N}^+\text{C}_\alpha\text{C}+\rho\text{COO}$	—	—	—
35	265	$\tau\text{C}_\beta\text{O}$	—	—	—
36	201	$\tau\text{C}_\alpha\text{N}^++\rho\text{CC}_\alpha\text{C}_\beta$	—	—	—
37	177	$\tau\text{C}_\alpha\text{N}^++\rho\text{CC}_\alpha\text{C}_\beta$	—	—	—
38	114	$\tau\text{C}_\alpha\text{C}_\beta$	—	—	—
39	65	$\tau\text{CC}_\alpha+\tau\text{CO}$	—	—	—

a. Ref. [26]

b. Ref. [30]

\* Numbers in the parentheses are from  
D,L-serine<sup>33</sup>

Table 6.7: Comparative calculated frequencies of the amino acid hydrochloride backbone

CYSH	SERH	GH <sup>a</sup>	GGH <sup>a</sup>	PED
3407	3412	3412	3436	$\nu\text{OH}$
3166	3155	3179	3161	$\nu\text{N}^+\text{H}$
3115	3132	3124	3109	$\nu\text{N}^+\text{H}$
3019	3045	3060	2964	$\nu\text{N}^+\text{H}$
1776	1744	1746	1738	$\nu\text{C}=\text{O}$
1634	1628	1616	1641	$\delta_{\text{as}}\text{N}^+\text{H}_3$
1614	1612	1610	1602	$\delta_{\text{as}}\text{N}^+\text{H}_3$
1481	1481	1512	1472	$\delta_{\text{s}}\text{N}^+\text{H}_3$
1348	1340	1378	1362	$\delta\text{COH}+\alpha\text{CH}_2$
1221	1249	1252	1247	$\nu\text{CO}+\delta\text{COH}$
1161	1174	1148	1155	$\nu\text{N}^+\text{H}_3$
1102	1144	1121	1126	$\nu\text{N}^+\text{H}_3$
1069	1094	1042	1050	$\nu\text{CN}^+$
732	728	657	661	$\nu\text{C}=\text{O}$
549	539	598	594	$\delta\text{COO}+\delta\text{N}^+\text{CC}$

a. Ref.[1]

Table 6.8: Comparative calculated frequencies of the amino acid hydrochloride sidechain

EtSH	CYSH	EtOH	SERH	PED
—	—	3336	3490	$\nu\text{OH}$
2932	3003	2920	3000	$\nu\text{CH}_2$
2902	2950	2877	2937	$\nu\text{CH}_2$
2571	2590	—	—	$\nu\text{SH}$
1434	1410	1494	1484	$\delta\text{CH}_2$
1273	1292	1277/ 1446	1225/ 1437	$\omega\text{CH}_2$
1251	1196	1318	1297	$\nu\text{CH}_2$
—	—	1051	1030	$\nu\text{C}-\text{O}$
737	779	799/ 1153	947/ 980	$\nu\text{CH}_2$
657	680	—	—	$\nu\text{CS}$



Table 6.9: (Continued): Non-redundant scaled force constants of CYSH

21	1	.002	2	-.005	3	.000	4	.002	5	-.276	6	-.002	7	-.008
	8	-.002	9	-.002	10	-.023	11	.041	12	.015	13	.065	14	-.006
	15	-.004	16	-.022	17	-.019	18	.011	19	-.028	20	.001	21	.553
22	1	.014	2	.006	3	-.001	4	.003	5	-.011	6	-.013	7	-.001
	8	-.001	9	.004	10	-.010	11	-.060	12	.053	13	.047	14	-.001
	15	.004	16	-.041	17	.011	18	-.009	19	.005	20	.004	21	.009
	22	.593												
23	1	.011	2	.002	3	.000	4	.003	5	.001	6	-.005	7	-.002
	8	.001	9	-.017	10	.031	11	.022	12	.058	13	-.090	14	.006
	15	.020	16	-.005	17	.017	18	.011	19	-.017	20	-.001	21	-.001
	22	-.009	23	.586										
24	1	.020	2	-.008	3	.004	4	-.007	5	.010	6	.011	7	.002
	8	-.001	9	-.042	10	.048	11	.052	12	-.053	13	-.008	14	.008
	15	.046	16	-.054	17	.062	18	.013	19	-.032	20	.002	21	-.004
	22	-.013	23	-.008	24	.740								
25	1	-.011	2	-.008	3	-.002	4	.006	5	.019	6	-.004	7	.006
	8	.003	9	-.026	10	.005	11	-.002	12	.102	13	-.021	14	.004
	15	-.063	16	-.040	17	-.008	18	-.034	19	.065	20	.002	21	-.008
	22	-.007	23	.030	24	-.005	25	.760						
26	1	.034	2	.000	3	.020	4	.011	5	-.084	6	.306	7	.001
	8	.003	9	-.613	10	.456	11	-.066	12	-.016	13	-.006	14	.070
	15	.067	16	.164	17	-.035	18	-.031	19	.010	20	.007	21	.025
	22	-.010	23	-.007	24	.008	25	.022	26	1.474				
27	1	-.016	2	.004	3	-.031	4	-.001	5	.085	6	.351	7	.005
	8	-.007	9	-.078	10	-.288	11	-.020	12	-.009	13	-.004	14	.054
	15	.066	16	.099	17	-.067	18	-.002	19	-.024	20	-.001	21	-.014
	22	-.002	23	.010	24	.003	25	-.016	26	.127	27	.916		
28	1	.007	2	.001	3	.001	4	.001	5	.016	6	.043	7	.002
	8	.000	9	.028	10	.208	11	.004	12	.003	13	.001	14	.131
	15	.005	16	-.015	17	-.015	18	-.001	19	-.002	20	.001	21	-.012
	22	.002	23	.007	24	.018	25	.004	26	.097	27	.115	28	.803
29	1	-.151	2	.056	3	.060	4	-.121	5	-.017	6	.004	7	.000
	8	.001	9	-.023	10	.006	11	-.001	12	-.002	13	.000	14	-.002
	15	-.019	16	.019	17	-.019	18	.012	19	-.003	20	-.015	21	.004
	22	-.004	23	-.003	24	-.001	25	.004	26	-.013	27	.005	28	-.002
	29	.537												
30	1	.228	2	.009	3	.030	4	-.254	5	.046	6	.011	7	-.006
	8	-.003	9	.020	10	.014	11	.000	12	-.011	13	-.003	14	.000
	15	.050	16	-.054	17	.014	18	-.017	19	-.003	20	-.045	21	-.007
	22	.001	23	.000	24	.009	25	-.001	26	.021	27	.001	28	.003
	29	-.013	30	.591										

Table 6.9: (Continued): Non-redundant scaled force constants of CYSH

31	1	.048	2	.106	3	-.058	4	-.012	5	-.061	6	-.003	7	-.010
	8	.021	9	-.020	10	.042	11	.001	12	.007	13	.005	14	-.003
	15	.017	16	.007	17	.008	18	-.011	19	-.019	20	.089	21	.007
	22	-.006	23	.009	24	-.026	25	-.001	26	.026	27	-.018	28	.001
	29	.002	30	.003	31	.787								
32	1	-.005	2	.017	3	-.044	4	.001	5	-.045	6	.008	7	-.004
	8	-.013	9	.000	10	.022	11	.002	12	.005	13	.004	14	-.001
	15	-.028	16	.009	17	-.115	18	-.003	19	.008	20	-.089	21	.002
	22	.010	23	-.007	24	-.023	25	-.006	26	.016	27	-.004	28	.003
	29	-.015	30	.018	31	.012	32	.572						
33	1	.354	2	-.054	3	-.029	4	.285	5	-.071	6	-.018	7	.030
	8	-.012	9	.030	10	-.032	11	-.007	12	.034	13	-.001	14	-.001
	15	.124	16	-.018	17	.088	18	.080	19	-.016	20	-.006	21	.029
	22	.016	23	.014	24	-.005	25	-.024	26	-.006	27	.006	28	-.001
	29	.016	30	.004	31	.026	32	-.033	33	1.044				
34	1	.003	2	-.002	3	-.002	4	.000	5	-.020	6	.049	7	.020
	8	-.005	9	.003	10	.001	11	-.012	12	.000	13	-.001	14	.002
	15	-.053	16	.008	17	.014	18	-.039	19	-.054	20	-.001	21	.001
	22	.004	23	-.009	24	.014	25	.000	26	.026	27	.034	28	.001
	29	.003	30	-.002	31	-.012	32	-.004	33	.010	34	.450		
35	1	.014	2	-.002	3	.007	4	-.017	5	.000	6	.006	7	.000
	8	.016	9	.004	10	-.001	11	-.002	12	.005	13	-.002	14	.002
	15	.018	16	.006	17	-.027	18	.003	19	-.002	20	-.014	21	.001
	22	-.020	23	.012	24	.009	25	.004	26	.000	27	.005	28	.001
	29	.006	30	.013	31	-.049	32	-.003	33	.049	34	-.005	35	.096
36	1	-.022	2	.002	3	.000	4	.008	5	-.018	6	-.027	7	.005
	8	.001	9	.003	10	-.017	11	-.017	12	-.033	13	.006	14	-.001
	15	-.022	16	-.029	17	-.011	18	.017	19	-.011	20	-.004	21	-.011
	22	-.030	23	.003	24	.009	25	.035	26	-.027	27	-.006	28	-.004
	29	-.001	30	-.001	31	.004	32	-.008	33	-.010	34	-.005	35	.019
37	36	.118												
	1	.100	2	-.017	3	-.005	4	.032	5	-.004	6	.018	7	-.008
	8	.029	9	-.007	10	.008	11	-.004	12	.011	13	.001	14	.000
	15	.059	16	-.010	17	.087	18	.000	19	-.041	20	.013	21	.005
	22	-.034	23	.027	24	.008	25	.005	26	.002	27	.005	28	.000
38	29	.017	30	.008	31	.081	32	-.043	33	.057	34	-.010	35	.046
	36	.022	37	.246										
	1	.015	2	-.002	3	.006	4	.004	5	.014	6	.015	7	-.005
	8	.010	9	-.040	10	.033	11	-.024	12	-.008	13	.000	14	.003
	15	.012	16	.088	17	.031	18	-.030	19	.016	20	.004	21	-.007
38	22	.008	23	-.025	24	.006	25	.001	26	.088	27	-.035	28	-.004
	29	-.001	30	-.003	31	.013	32	.002	33	-.001	34	-.001	35	.008
	36	-.008	37	.021	38	.090								



Table 6.9: (Continued): Non-redundant scaled force constants of CYSH

39	1	-.001	2	.001	3	.000	4	-.001	5	.002	6	-.010	7	-.002
	8	.000	9	-.003	10	.008	11	.003	12	.003	13	.000	14	.001
	15	.004	16	-.008	17	-.006	18	.007	19	.010	20	.001	21	.000
	22	.000	23	.000	24	-.001	25	-.001	26	-.005	27	-.001	28	.003
	29	-.001	30	.000	31	.001	32	.002	33	-.002	34	-.013	35	-.003
	36	.000	37	-.004	38	.001	39	.158						

Table 6.10: Non-redundant scaled force constants of SERH

1	1	4.558												
2	1	.068	2	4.802										
3	1	.035	2	.041	3	4.891								
4	1	.382	2	.185	3	.142	4	4.986						
5	1	.210	2	.020	3	-.024	4	.004	5	4.857				
6	1	.168	2	.005	3	-.016	4	-.027	5	.172	6	5.156		
7	1	.044	2	-.014	3	.007	4	.002	5	.065	6	.052	7	4.849
8	1	-.008	2	-.009	3	-.003	4	-.027	5	.000	6	.002	7	.000
	8	6.804												
9	1	-.047	2	.016	3	-.005	4	.064	5	.035	6	.501	7	-.003
	8	-.007	9	11.578										
10	1	-.000	2	.006	3	.011	4	.007	5	.005	6	.258	7	.003
	8	-.003	9	1.159	10	7.267								
11	1	.003	2	-.002	3	-.002	4	.006	5	.070	6	-.037	7	-.015
	8	.003	9	-.033	10	.002	11	5.460						
12	1	-.012	2	-.000	3	-.003	4	-.006	5	.026	6	-.007	7	.009
	8	.002	9	-.004	10	-.013	11	.023	12	5.426				
13	1	-.030	2	.005	3	.004	4	-.059	5	.095	6	-.018	7	-.001
	8	-.008	9	.004	10	-.012	11	.015	12	.011	13	5.252		
14	1	.009	2	.001	3	.002	4	-.009	5	-.002	6	-.016	7	.004
	8	.003	9	-.088	10	.144	11	.001	12	.002	13	.002	14	6.519
15	1	.144	2	.002	3	.017	4	.015	5	.227	6	.263	7	-.098
	8	.006	9	.039	10	-.004	11	-.037	12	.012	13	-.015	14	.005
	15	.963												
16	1	-.298	2	-.006	3	.012	4	-.087	5	.242	6	.361	7	.002
	8	-.006	9	.060	10	.016	11	-.042	12	-.029	13	.005	14	.006
	15	.193	16	1.313										
17	1	.235	2	-.008	3	.021	4	-.010	5	.361	6	-.102	7	.015
	8	.010	9	-.076	10	-.021	11	-.029	12	.002	13	-.013	14	-.001
	15	.185	16	-.175	17	1.120								
18	1	.180	2	.018	3	-.013	4	-.017	5	-.168	6	-.085	7	-.013
	8	-.000	9	-.025	10	-.002	11	-.006	12	.015	13	.004	14	.000
	15	.034	16	-.024	17	.002	18	.622						



Table 6.10: (Continued): Non-redundant scaled force constants of SERR

30	1	.226	2	.007	3	.010	4	-.416	5	.049	6	-.017	7	.007
	8	.030	9	.005	10	.017	11	-.002	12	-.000	13	-.017	14	.002
	15	.012	16	-.035	17	.064	18	.034	19	-.000	20	.008	21	-.010
	22	-.002	23	-.001	24	-.004	25	.003	26	.004	27	.007	28	.002
	29	-.008	30	.697										
31	1	.079	2	.083	3	-.073	4	.059	5	-.073	6	-.021	7	.039
	8	.007	9	-.008	10	.003	11	.001	12	-.005	13	-.004	14	-.000
	15	-.058	16	.008	17	.019	18	.061	19	.026	20	.004	21	.013
	22	.020	23	.006	24	.003	25	-.011	26	-.002	27	-.003	28	.000
	29	-.007	30	.012	31	.753								
32	1	-.011	2	.043	3	-.040	4	-.032	5	-.042	6	-.015	7	.012
	8	-.004	9	.015	10	-.012	11	.005	12	-.001	13	.007	14	-.001
	15	-.064	16	.048	17	-.084	18	.052	19	-.005	20	-.010	21	.001
	22	-.007	23	-.004	24	.010	25	-.014	26	.004	27	-.005	28	-.001
	29	-.002	30	.014	31	-.068	32	.735						
33	1	.543	2	-.045	3	-.042	4	.611	5	-.086	6	.030	7	-.029
	8	.054	9	.056	10	.050	11	-.013	12	-.012	13	-.036	14	-.005
	15	.085	16	-.154	17	.080	18	-.059	19	.040	20	.083	21	.039
	22	.006	23	-.025	24	.027	25	.003	26	-.019	27	.048	28	-.002
	29	-.027	30	.123	31	.110	32	-.029	33	1.607				
34	1	-.012	2	-.004	3	-.009	4	-.010	5	-.002	6	.000	7	.016
	8	-.001	9	.012	10	.009	11	.009	12	-.000	13	-.000	14	.001
	15	-.061	16	.031	17	.048	18	-.027	19	-.052	20	-.005	21	.004
	22	-.007	23	.003	24	-.013	25	.007	26	.001	27	.001	28	-.000
	29	.002	30	-.003	31	-.004	32	-.002	33	-.025	34	.438		
35	1	-.009	2	-.002	3	-.003	4	.003	5	.010	6	.001	7	-.003
	8	-.007	9	.000	10	.004	11	.002	12	-.000	13	.002	14	-.000
	15	-.006	16	.004	17	-.013	18	.001	19	-.002	20	.016	21	-.005
	22	-.002	23	.001	24	-.003	25	-.007	26	-.001	27	.002	28	-.000
	29	-.001	30	.002	31	-.028	32	.010	33	-.002	34	.000	35	.031
36	1	-.021	2	.002	3	.003	4	-.002	5	-.042	6	-.028	7	.007
	8	-.003	9	-.016	10	.018	11	-.042	12	.010	13	-.018	14	-.001
	15	-.009	16	.001	17	-.035	18	-.008	19	-.010	20	-.001	21	-.009
	22	.064	23	.025	24	.017	25	.005	26	.002	27	-.014	28	-.004
	29	-.002	30	-.004	31	.009	32	-.004	33	-.008	34	.003	35	-.004
	36	.080												
37	1	-.233	2	.018	3	.006	4	-.052	5	.020	6	.015	7	-.005
	8	-.003	9	.016	10	-.006	11	.004	12	.008	13	.004	14	-.000
	15	.014	16	.046	17	-.103	18	-.027	19	-.039	20	-.006	21	-.011
	22	-.036	23	-.013	24	.001	25	-.001	26	.016	27	-.005	28	-.001
	29	.002	30	-.034	31	-.071	32	.016	33	-.140	34	.010	35	.010
	36	-.018	37	.170										

Table 6.10: (Continued): Non-redundant scaled force constants of SERH

38	1	-.002	2	.004	3	-.013	4	.008	5	.023	6	.007	7	.016
	8	-.002	9	-.014	10	.006	11	-.032	12	.002	13	-.014	14	.000
	15	.093	16	-.067	17	-.008	18	.042	19	-.012	20	.001	21	-.018
	22	.001	23	-.021	24	.026	25	-.022	26	.006	27	.009	28	.004
	29	-.006	30	.003	31	-.003	32	.005	33	.004	34	.014	35	-.001
	36	-.047	37	.008	38	.173								
39	1	-.003	2	.002	3	-.001	4	-.003	5	.013	6	.007	7	.003
	8	.000	9	-.001	10	-.010	11	-.001	12	.001	13	-.015	14	-.001
	15	.022	16	-.046	17	.009	18	.017	19	-.010	20	.000	21	-.008
	22	-.013	23	-.007	24	-.001	25	-.016	26	.008	27	-.000	28	.006
	29	.001	30	.000	31	-.000	32	.001	33	-.001	34	.002	35	-.000
	36	-.031	37	.002	38	.078	39	.073						

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## Chapter 7

# Vibrational Analysis of Glycine Zwitterion

In this chapter, vibrational analysis of the smallest amino acid, glycine (Gly) is presented using Onsager reaction field approach. A complete set of scale factors is obtained for this important amino acid by using the fitting procedure described in chapter 3.

Gly, the smallest member of the amino acid family was the center of attention of many investigations [1-22]. Gly is one of the non essential amino acids and most commonly found in proteins along with leucine and serine. Gly is one of the three amino acids essential for the biosynthesis of the non-proteinic nitrogenous material, creatine, in human and animal tissues. Gly and succinyl CoA are the starting compounds in heme synthesis. Its role in the genesis of nucleotide purine ring as one of the important amino acids cannot be augmented [23].

The experimental IR and Raman spectra of Gly in solution phase is very limited [24,25]. This is because in aqueous solution, the absorption due to the water molecules, especially in the mid IR range, interferes with that of Gly. As a result most of the recent spectroscopic studies of Gly are based on  $\alpha$  crystalline form [26-28]. Another important point is that since there is no chiral carbon atom in Gly, the more accurate solution phase VCD and ROA measurements are not available. As a result the correct interpretation of the available solution and/or solid phase experimental spectra requires a good theoretical model.

The structure of Gly is completely different in the gas and liquid phases. In gas phase it exhibits a non-ionic structure ( $\text{NH}_2\text{CH}_2\text{COOH}$ ), whereas in the liquid or solid it exists



as a zwitterion ( $\text{N}^+\text{H}_3\text{CH}_2\text{COO}^-$ ). The *ab initio* potential energy surface (PES) of gaseous Gly has been studied extensively [1-14]. But the theoretical studies on Gly zwitterion are relatively few [20-22]. Attempts to study the isolated Gly zwitterion using *ab initio* methods have not been successful so far because the calculation of isolated Gly zwitterion either goes to the gas phase structure or even when optimized restrictively generates imaginary frequency. For example, attempts to deduce the *ab initio* force field on the Gly zwitterion crystal geometry retains the residual linear forces because this is not a true minima in the PES [20]. Here we show that the choice of appropriate basis set can reach the right minima in the PES but suffer from the intramolecular H-bonding problem which is absent in solid or solution phase. As a result such *ab initio* calculation on isolated molecule cannot reproduce the true features of experimental vibrational spectra. The extra stability of amino acid zwitterion in the solution or solid phase over the gas phase, comes through the interaction with the solvent and through the intermolecular interactions. Thus the effect of the solvent environment and the intermolecular H-bonding cannot be ignored in the theoretical calculation of amino acid zwitterion. Two different theoretical approaches have emerged for the improvement of the *ab initio* model in this regard; the supermolecular approach and the Onsager reaction field model. As discussed in chapter 5, the supermolecular approach although produces improved results over the *ab initio* force field, difficult to generalize to higher systems. This is because with the increase in the number of atoms, the number of water molecules also increases and hence becomes computationally intensive. Also the PEDs get mixed up with the water modes and is difficult to separate. Using the more general Onsager reaction field approach with judicious choice of basis set and the radius of the molecular volume at a particular dielectric medium appears to give the more appropriate solution for describing the amino acid zwitterions.

Thus in this chapter our endeavour is to present a solvated Gly zwitterion calculation with an appropriate choice of basis set and the radius of the cavity (which is achieved on a trial and error basis) which will produce the equivalent of inter-molecular H-bonded environment in the condensed phase of Gly zwitterion. Different basis sets (4-21G, 6-31G\*, 6-31+G, 6-31++G, 6-31++G\* and 6-31++G\*\*), are used to select 6-31++G\* as the right one

for the Onsager model of the Gly zwitterion. Also a complete set of nonredundant force constants for Gly based on the solvated ab initio calculation is presented.

## 7.1 Calculations

The ab initio force constants and frequencies of Gly were calculated analytically at the optimized geometry. The recommended ab initio radius of solvent model is reduced by 0.5 Å for all the calculations unless otherwise mentioned. The cartesian force constant matrix was transformed to the nonredundant local coordinate. The nonredundant local coordinates of Gly are given in Table-7.1 and Figure 7.1. The fitting procedure described in detail in chapter 3 is used to get the force field of Gly by fitting four different isotopomers. The fitting produced an average deviation of 7.9 cm<sup>-1</sup> from the available experimental data.

## 7.2 Results

### 7.2.1 Geometry

The optimized geometry of solvated Gly obtained by using different basis sets is shown in Table-7.2 along with the crystal structure [29], molecular dynamics (MD) simulated structure [20] and the calculated HF/6-31++G\* isolated zwitterion structure. Table-7.2 clearly indicates that the ab initio calculated structure is slightly different from the experimental structure. Even if the optimization is done at its full degree of freedom, the ab initio model produces a structure closer to planar symmetric (Cs) compared to the crystal geometry irrespective of the basis set. In the crystal structure all the three N<sup>+</sup>H bond lengths are quite different (1.054, 1.037 and 1.025), with the planar N<sup>+</sup>H slightly longer than the other two. This may be due to different extent of H-bonding experienced by each N<sup>+</sup>H bond in the crystal environment. In the ab initio calculation, both the out of plane N<sup>+</sup>H bond lengths are the same in isolated as well as solvated calculations. But the only improvement introduced through the solvent model is the relative difference between the planar and nonplanar N<sup>+</sup>H gets reduced significantly. In the isolated model the intramolecular H-bonding is more pronounced and hence the planar N<sup>+</sup>H bond length

(1.053) is much longer than the solvated one (1.020). The CC and CN<sup>+</sup> bond lengths are overestimated and do not change much from the isolated model. Both the CO bond lengths are exactly the same in the crystal structure due to the equal extent of H-bonding with the neighbouring N<sup>+</sup>H<sub>3</sub> groups and calculations for the different basis sets produce results close to this. The calculated bond angles for various basis sets are relatively of the same order but 6-31++G\* produces slightly improved results over others. The low value of the C(2)-N<sup>+</sup>(1)-H(3) (planar) angle (98.9°) in the isolated model is probably due to the formation of a five membered ring through intramolecular H-bonding. The 4-21G and 6-31++G\*\* basis sets in solvated model produce structures oriented differently from the other basis sets and are closer to the isolated structure. The optimized structures in isolated and solvated models at 6-31++G\* basis set along with the X-ray structure are shown in Figure 7.2.

### 7.2.2 Selection of the right model

The aim of the present work is to choose a suitable ab initio model for proper description of the features of the experimental vibrational spectra of amino acids, using Gly as a test case. The existing literature on the vibrational spectra of amino acids and their isotopomers infer the following general observations.

- i) In most of the solution or solid state spectra N<sup>+</sup>H<sub>3</sub> asymmetric bend and CO asymmetric stretch appear at around 1600 cm<sup>-1</sup>, the first one appearing at a higher frequency.
- ii) N<sup>+</sup>H<sub>3</sub> symmetric bend appears next at around 1520 cm<sup>-1</sup>, followed by CO symmetric stretch at around 1400 cm<sup>-1</sup>. The 1400 cm<sup>-1</sup> is confirmed to be CO stretch because of its invariance to isotopic substitution. Also, in alanine the more accurate VCD spectra show the same difference of around 200 cm<sup>-1</sup> between the two CO stretches.
- iii) Most of the other band positions vary depending on the structure of the amino acids.

**Criterion 1:** The sensitive frequencies obtained from different basis sets in solvated model are given in Table-7.3 along with their PEDs. The PEDs match with the expected order for  $\delta_a$ N<sup>+</sup>H<sub>3</sub>,  $\nu_a$ CO and  $\delta_s$ N<sup>+</sup>H<sub>3</sub> as discussed above only for 6-31++G\* basis set.

**Criterion 2:** The radii used in the solvated model for different basis sets are reduced by 0.5 Å from the recommended value since the recommended one corresponds to a value increased by 0.5 Å from the actual computed value [30]. Although criterion 1 is met by 6-31++G\* basis set, criterion 2 i.e.  $\nu_s\text{CO}$  should appear as a major component below  $\delta_s\text{N}^+\text{H}_3$  is not fulfilled properly. So we investigated the effect of the cavity radius on the PEDs. We tried different possibilities and the best model appears to be the one corresponding to a value 3.2 Å as shown in Table-7.3 [31].

After fitting to the experimental frequencies of the four different isotopomers, the fitted force constants produced excellent description of the different normal modes as shown in Tables-7.4 and 7.5.

### 7.2.3 Vibrational Frequencies

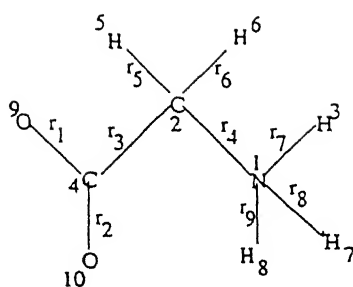
Fitted frequencies of Gly-d<sub>0</sub> is given in Table-7.4 along with their PEDs. Table-7.5 contains the calculated frequencies of different isotopomers. The fitted frequencies are in excellent agreement with the experimental frequencies except for the lowest three, mainly torsions and skeletal deformations. Ab initio model is known to be very poor for these modes. Thus we excluded these numbers in calculating the average error. Our fitted PEDs match very well with the earlier reported PEDs obtained by using the MD simulated force field, [20] with few exceptions. In the fitting we used the experimental data from both crystal and solution spectra. The N<sup>+</sup>H and CH frequencies were overestimated significantly in the earlier work, [20] while the present numbers are in good agreement. In this region we choose all bands from the crystal spectra except for 3011 cm<sup>-1</sup> which is from the solution Gly-d<sub>0</sub>. Both the  $\delta_a\text{N}^+\text{H}_3$  appear above  $\nu\text{CO}$  followed by  $\delta_s\text{N}^+\text{H}_3$  in the Gly-d<sub>0</sub> spectra as expected. All these four bands are calculated at 1645, 1624, 1595 and 1523 cm<sup>-1</sup> and get shifted to 1174, 1167, 1588 and 1205 cm<sup>-1</sup> in Gly-N<sup>+</sup>D<sub>3</sub>, 1643, 1622, 1592 and 1522 cm<sup>-1</sup> in Gly-CD<sub>2</sub> and 1176, 1168, 1585 and 1208 cm<sup>-1</sup> in Gly-N<sup>+</sup>D<sub>3</sub>CD<sub>2</sub> spectra. The  $\delta\text{CH}_2$  and  $\nu\text{CO}$  modes give a better fit with the 1440 and 1410 cm<sup>-1</sup> solution phase frequencies and so these are used for the fitting. This 1410 cm<sup>-1</sup>  $\nu\text{CO}+\nu\text{CC}$  mode remain invariant in different isotopomers as expected. The 1327 cm<sup>-1</sup> solution band matches very well with

our fitted frequency of  $1326\text{ cm}^{-1}$  and is assigned to  $t\text{CH}_2 + \rho\text{CH}_2$ . This band gets shifted to  $1316, 935, 930\text{ cm}^{-1}$  in Gly- $\text{N}^+\text{D}_3$ , Gly- $\text{CD}_2$  and Gly- $\text{N}^+\text{D}_3\text{CD}_2$  respectively. The  $1138$  and  $1119\text{ cm}^{-1}$  bands are both assigned as mixed modes of  $\rho\text{N}^+\text{H}_3$ ,  $t\text{CH}_2$  and  $\rho\text{CH}_2$ . These two bands shift in isotopic spectra to  $821, 763\text{ cm}^{-1}$  in  $\text{N}^+\text{D}_3$ ,  $1215, 1178\text{ cm}^{-1}$  in  $\text{CD}_2$  and  $807$  and  $707\text{ cm}^{-1}$  in  $\text{N}^+\text{D}_3\text{CD}_2$  spectra respectively. The  $1037\text{ cm}^{-1}$  crystal band is used for  $\nu\text{CN}^+$  mode in Gly- $\text{d}_0$  and it agrees very well with our  $1039\text{ cm}^{-1}$  band. The  $\delta\text{COO} + \delta\text{CCN}^+ + \rho\text{COO}$  mixed mode could be assigned to either  $704\text{ cm}^{-1}$  from the crystal spectra or to  $665\text{ cm}^{-1}$  from the solution in Gly- $\text{d}_0$ . Earlier SQM assignment matches well with the solution phase value. Our fitting produces this band at  $668\text{ cm}^{-1}$  and is in support to the earlier SQM assignment. This frequency gets shifted to  $634, 646, 618\text{ cm}^{-1}$  respectively in the other three isotopomers, in good agreement with the expected experimental fundamentals confirming the assignment.

The non redundant fitted force constants of Gly is given in Table-7.6.

### 7.3 Conclusions

The Onsager reaction field approach is found to be very successful in reproducing the vibrational spectra of the smallest amino acid, Gly. The selection of basis set and the radius of the molecular volume is considered as two prime factors for mimicking the experimental spectra within this model. The fitting procedure to obtain the scale factors from the ab initio force field of Gly has shown to be very successful giving an average deviation of  $7.9\text{ cm}^{-1}$  between the predicted and the experimental frequencies for four isotopomers. A complete set of non redundant force constants were obtained for Gly. The excellent agreement between the fitted and experimental frequencies clearly implies that the methodology could, in principle, be applied successfully to other amino acids.



$a_1 = \text{O}(9)\text{-C}(4)\text{-O}(10)$ ,  $b_1 = \text{C}(2)\text{-C}(4)\text{-O}(10)$ ,  $b_2 = \text{C}(2)\text{-(4)-O}(10)$   
 $a_2 = \text{H}(5)\text{-C}(2)\text{-H}(6)$ ,  $a_3 = \text{C}(4)\text{-C}(2)\text{-H}(5)$ ,  $a_4 = \text{C}(4)\text{-C}(2)\text{-H}(6)$   
 $b_3 = \text{N}(1)\text{-C}(2)\text{-H}(5)$ ,  $b_4 = \text{N}(1)\text{-C}(2)\text{-H}(6)$ ,  $b_5 = \text{N}(1)\text{-C}(2)\text{-C}(4)$   
 $a_5 = \text{H}(3)\text{-N}(1)\text{-H}(7)$ ,  $a_6 = \text{H}(3)\text{-N}(1)\text{-H}(8)$ ,  $a_7 = \text{H}(7)\text{-N}(1)\text{-H}(8)$   
 $b_6 = \text{C}(2)\text{-N}(1)\text{-H}(3)$ ,  $b_7 = \text{C}(2)\text{-N}(1)\text{-H}(7)$ ,  $b_8 = \text{C}(2)\text{-N}(1)\text{-H}(8)$

Figure 7.1: Internal coordinates of Gly.

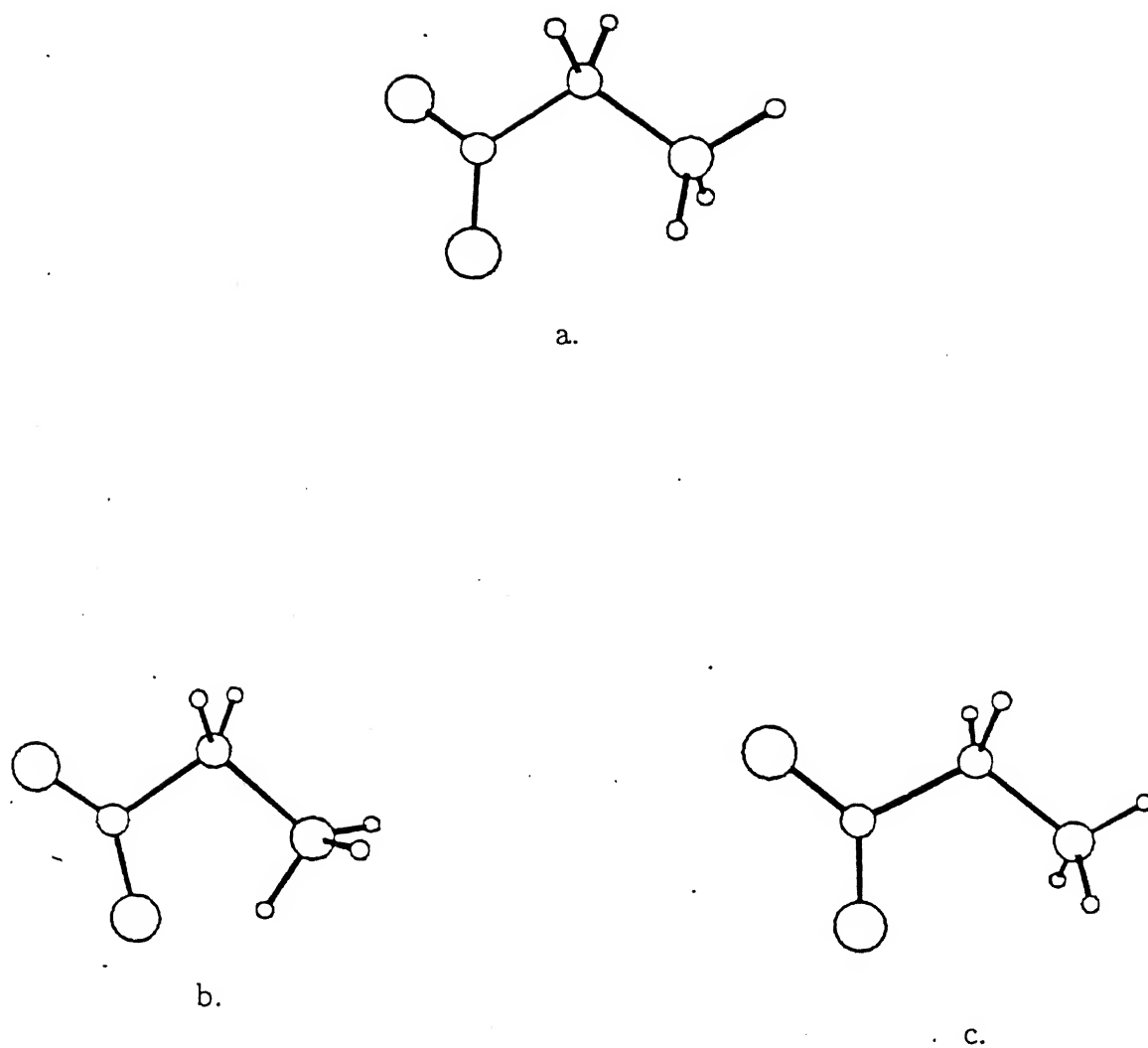


Figure 7.2: Structure of X-ray and optimized Gly using 6-31++G\* basis set.  
a) X-ray structure b) isolated c) solvated with radius 3.2 Å

Table 7.1: Local symmetry coordinates<sup>a</sup> of Gly

$S_{1-9} =$	$r_{1-9}$ (all stretch)	$S_{17} =$	$a_5 + a_6 + a_7 - b_6 - b_7 - b_8$ ( $\delta_s N^+ H_3$ )
$S_{10} =$	$2a_1 - b_1 - b_2$ ( $\delta COO$ )	$S_{18} =$	$2a_7 - a_5 - a_6$ ( $\delta_a N^+ H_3$ )
$S_{11} =$	$b_1 - b_2$ ( $\delta COO$ )	$S_{19} =$	$a_5 - a_6$ ( $\delta_a N^+ H_3$ )
$S_{12} =$	$4a_2 - a_3 - a_4 - b_3 - b_4$ ( $\delta CH_2$ )	$S_{20} =$	$2b_6 - b_7 - b_8$ ( $\rho N^+ H_3$ )
$S_{13} =$	$a_3 + a_4 - b_3 - b_4$ ( $\omega CH_2$ )	$S_{21} =$	$b_7 - b_8$ ( $\rho N^+ H_3$ )
$S_{14} =$	$a_3 - a_4 + b_3 - b_4$ ( $\rho CH_2$ )	$S_{22} =$	$\gamma_{24910}$ ( $\gamma CO$ )
$S_{15} =$	$a_3 - a_4 - b_3 + b_4$ ( $tCH_2$ )	$S_{23} =$	$\tau_{24}$ ( $\tau CC$ )
$S_{16} =$	$5b_5 - a_2 - a_3 - a_4 - b_3 - b_4$ ( $\delta CCN^+$ )	$S_{24} =$	$\tau_{21}$ ( $\tau CN^+$ )

a. Internal coordinate numberings are according to Figure 7.1.



Table-7.2: Optimized geometries of Gly at different basis sets\*

Internal <sup>a</sup> coord.	Solvated zwitterion at different basis sets						Molecular <sup>b</sup> dynamics	Crystal <sup>c</sup>	Isolated 6-31++G*
	4-21G	6-31G*	6-31++G		6-31++G**				
			6-31+G	6-31++G*	3.1	3.2			
N1-C2	1.527	1.504	1.514	1.510	1.502	1.501	1.502	1.476	1.504
N1-H3	1.041	1.024	1.032	1.024	1.020	1.018	1.014	1.054	1.053
N1-H7	1.017	1.011	1.013	1.011	1.011	1.010	1.013	1.037	1.005
N1-H8	1.017	1.011	1.013	1.011	1.011	1.010	1.010	1.025	1.005
C2-H5	1.078	1.080	1.081	1.080	1.080	1.080	1.079	1.089	1.079
C2-H6	1.078	1.080	1.081	1.080	1.080	1.080	1.081	1.090	1.079
C2-C4	1.575	1.559	1.560	1.546	1.553	1.552	1.552	1.526	1.566
C4-O9	1.259	1.226	1.252	1.252	1.228	1.229	1.231	1.250	1.245
C4-O10	1.245	1.252	1.305	1.290	1.250	1.244	1.240	1.250	1.207
C2-N1-H3	113.5	111.8	110.3	110.9	111.9	112.3	113.2	112.1	98.9
C2-N1-H7	101.2	113.5	115.2	113.7	112.9	112.0	108.6	111.7	114.0
C2-N1-H8	113.5	113.5	115.2	113.7	112.9	112.4	112.8	110.4	114.0
N1-C2-H5	109.1	106.4	106.1	106.8	106.8	107.2	108.4	105.3	109.6
N1-C2-H6	109.1	106.4	106.1	106.8	106.8	107.0	107.5	105.4	109.6
N1-C2-C4	106.6	117.0	121.0	117.4	115.0	113.5	112.1	111.8	105.4
C2-C4-O9	113.8	126.8	122.9	120.6	118.0	117.0	116.3	114.7	112.0
C2-C4-O10	116.5	118.9	115.2	115.2	114.4	114.5	114.8	113.8	115.0
H3-N1-C2-H5	119.2	56.9	56.5	57.2	57.4	62.5	93.1	48.5	-119.8
H7-N1-C2-H5	-120.9	176.2	173.9	175.9	177.3	-177.1	-145.3	169.4	123.0
H8-N1-C2-H5	-1.1	-62.3	-60.8	-61.6	-62.5	-58.1	-26.8	-72.1	-2.7
H3-N1-C2-H6	1.1	-57.0	-56.6	-57.2	-57.6	-53.4	-23.5	-65.1	119.8
H3-N1-C2-C4	-119.8	179.9	180.0	180.0	179.8	-175.2	-143.6	170.3	-0.0
N1-C2-C4-O9	-0.0	-0.0	-0.0	-0.0	-0.0	2.1	7.1	18.9	-0.0
N1-C2-C4-O10	-180.0	180.0	180.0	180.0	-179.9	-178.3	-171.2	-161.8	180.0

a. Bond lengths are in Å and angles are in rad.

b. Ref. [20]

c. Ref. [29]

\* The recommended radius in Gaussian-94 is reduced by 0.5 Å in different basis set calculations. In 6-31++G\*, this corresponds to 3.1 (see text).

Table-7.3: Selective unscaled vibrational frequencies of solvated Gly at different basis sets\*

Table-7.3: Selective unscaled vibrational frequencies of solvated Gly at different basis sets										
Expt. <sup>a</sup>	4-21G		6-31G*		6-31+G		6-31++G		6-31+++G**	
1634	1842	$\delta_a N^+H_3$	1848	$\nu CO$	1830	$\delta_a N^+H_3$	1838	$\delta_a N^+H_3$	1817	$\nu CO$
1618	1840	$\delta_a N^+H_3 + \nu CO$	1812	$\delta_a N^+H_3$	1827	$\delta_a N^+H_3 + \delta_s N^+H_3$	1836	$\delta_a N^+H_3$	1804	$\delta_a N^+H_3$
1597	1817	$\nu CO + \delta_a N^+H_3$	1809	$\delta_a N^+H_3$	1776	$\delta_s N^+H_3 + \delta_a N^+H_3$	1774	$\delta_s N^+H_3$	1776	$\delta_a N^+H_3$
		$\delta_s N^+H_3$								
1533	1646	$\delta_s N^+H_3 + \delta CH_2$	1708	$\delta_s N^+H_3$	1640	$\nu CO + \delta CH_2$	1648	$\nu CO + \delta CH_2$	1645	$\delta_s N^+H_3$
		$\omega CH_2$								
1410	1467	$\omega CH_2$	1566	$\omega CH_2 + \nu CO$	1532	$\omega CH_2 + \nu CO$	1541	$\omega CH_2 + \nu CO$	1548	$\omega CH_2 + \nu CO$
				$\nu CC$		$\nu CC$		$\nu CO$		$\nu CO$
1138	1227	$\rho N^+H_3 + \omega CH_2$	1197	$tCH_2 + \rho CH_2$	1238	$\rho N^+H_3 + tCH_2$	1232	$\rho N^+H_3 + tCH_2$	1189	$tCH_2 + \rho CH_2$
				$\rho N^+H_3 + \gamma CO$		$\rho CH_2$		$\rho CH_2$		$\rho N^+H_3 + \gamma CO$
1119	1191	$\rho N^+H_3 + tCH_2$	1164	$\rho N^+H_3 + \omega CH_2$	1202	$\rho N^+H_3$	1208	$\rho N^+H_3 + \omega CH_2$	1169	$\rho N^+H_3 + \omega CH_2$
		$\rho CH_2$								
Expt. <sup>a</sup>	6-31++G*(3.1)		6-31++G*(3.6)		6-31++G*(3.35)		6-31++G*(3.2)			
1634	1818	$\delta_a N^+H_3(80)$	1860	$\nu CO(84)$	1835	$\nu CO(48) + \delta_a N^+H_3(42)$	1824	$\delta_a N^+H_3(63) + \nu CO(28)$		
1618	1805	$\delta_a N^+H_3(94)$	1836	$\delta_a N^+H_3(96)$	1832	$\delta_a N^+H_3(52) + \nu CO(38)$	1806	$\delta_a N^+H_3(74)$		
1597	1790	$\nu CO(74)$	1813	$\delta_a N^+H_3(81)$	1804	$\delta_a N^+H_3(70)$	1799	$\nu CO(52) + \delta_a N^+H_3(32)$		
1533	1699	$\delta_s N^+H_3(79)$	1642	$\delta_s N^+H_3(65) + \delta CH_2(17)$	1662	$\delta_s N^+H_3(77)$	1695	$\delta_s N^+H_3(83)$		
1410	1564	$\omega CH_2(40) + \nu CC(18)$	1534	$\nu CO(45) + \nu CC(20)$	1549	$\nu CO(37) + \omega CH_2(24)$	1563	$\omega CH_2(35) + \nu CO(29)$		
		$\nu CO(15)$		$\omega CH_2(16)$		$\nu CC(20)$		$\nu CC(19)$		
1138	1198	$\rho N^+H_3(31) + tCH_2(28)$	1188	$\rho N^+H_3(28) + tCH_2(27)$	1194	$\rho N^+H_3(37) + tCH_2(26)$	1194	$tCH_2(30) + \rho N^+H_3(29)$		
		$\rho CH_2(25) + \gamma CO(14)$		$\rho CH_2(21) + \gamma CO(12)$		$\rho CH_2(22) + \gamma CO(12)$		$\rho CH_2(25) + \gamma CO(14)$		
1119	1170	$\rho N^+H_3(64) + \omega CH_2(13)$	1181	$\rho N^+H_3(67) + \omega CH_2(12)$	1176	$\rho N^+H_3(64) + \omega CH_2(12)$	1172	$\rho N^+H_3(62) + \omega CH_2(13)$		

a. Ref. [24,25]

\* The recommended radius in Gaussian-94 is reduced by 0.5 Å in different basis set calculations. In 6-31++G\*, this corresponds to 3.1 (see text).





Table 7.6: (Continued): The symbolic F matrix of Gly in local coordinates

-0.432	-0.025	-0.022	0.016	0.004	0.005	-0.032	0.057	0.068
0.632	0.002	-0.001	0.000	0.001	0.089	-0.093	0.005	0.023
-0.029	-0.001	0.001	-0.002	0.003	0.949	0.001	0.001	0.000
0.004	-0.003	0.002	-0.002	-0.011	0.009	-0.000	0.007	0.001
-0.004	-0.196	0.606	-0.058	0.072	0.144	0.076	-0.051	-0.035
-0.013	-0.049	-0.046	-0.010	-0.179	0.017	0.038	-0.003	-0.002
1.079	-0.036	0.038	0.014	-0.258	-0.011	-0.011	0.069	0.067
0.075	-0.008	0.052	0.011	0.027	-0.002	-0.002	0.031	0.565
0.020	-0.028	-0.044	-0.039	-0.001	-0.002	-0.074	0.050	0.042
0.018	-0.041	0.004	0.006	0.003	-0.003	-0.039	0.018	0.594
-0.007	0.003	0.004	0.003	-0.001	0.001	-0.006	0.067	-0.072
-0.001	0.006	-0.000	0.001	-0.041	-0.001	0.013	-0.003	0.002
0.623	-0.007	0.081	0.034	-0.002	-0.002	-0.004	-0.008	-0.006
0.004	-0.022	-0.010	0.033	0.036	-0.000	-0.003	0.100	-0.021
0.008	-0.001	0.738	0.003	-0.008	-0.006	-0.001	0.006	-0.005
-0.003	0.008	-0.000	0.002	-0.003	-0.001	-0.001	0.070	-0.071
-0.006	0.003	-0.002	0.043	0.001	0.664	0.002	0.002	-0.001
0.000	0.020	-0.021	-0.001	-0.003	0.008	0.003	0.002	0.002
-0.002	0.044	0.070	0.003	0.001	0.002	0.019	0.001	-0.009
0.532	-0.004	0.003	-0.002	0.004	0.014	-0.014	-0.000	-0.023
0.012	0.001	0.008	-0.002	-0.000	-0.111	0.009	0.004	-0.003
-0.006	-0.009	-0.003	0.023	0.074	0.105	-0.005	0.005	-0.002
-0.011	0.003	0.001	0.005	-0.008	-0.008	0.001	0.000	0.001
0.005	-0.003	-0.010	0.004	-0.002	-0.004	-0.060	-0.008	0.019
0.007	-0.028	0.024						

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## Chapter 8

# Theoretical Prediction of the Vibrational spectra of Cysteine and Serine Zwitterions

There have been a number of ab initio studies of the gas phase vibrational analysis of amino acids, such as glycine [1], alanine (Ala) [2], cysteine (Cys), serine (Ser) [3], and proline [4]. In the zwitterionic form a solvated model of glycine was used to obtain the vibrational frequencies and assignments as described in chapter 7. A good number studies of Ala in the solid state in both IR and Raman spectroscopy is available in the literature [5-18]. Ala being the smallest chiral amino acid, was the subject of interest for VCD and ROA spectra [2,19,20]. A complete vibrational assignment based on VCD spectra using Urey-Bradeley force field of Ala in solution was first presented by Diem et al. [20]. The ab initio calculations of isolated molecule [2] and more recently the Onsager reaction field model [19] were used to assign the experimental vibrational spectra of Ala zwitterion in the region 800 to 1600  $\text{cm}^{-1}$ . Ab initio isolated model calculations of Cys and Ser were used to assign their experimental spectra [21]. The previous quantum mechanical calculations of Cys include studies of protonation and ionization potential [22], a comparison of PCILO and SCF results [23] and minimum energy conformations [24]. Calculations of Ser include studies of protonation [23,25,26], lattice energies [27], energy differences of enantiomers [28,29], crystal and peptide structures [30] and low energy conformations [31,32]. The thiol group in the Cys residue side chain is responsible for the stabilization of the secondary structure of proteins and hence was the subject of a number of spectroscopic studies for

characterizing its conformers (chapter 6). In the experimental side, solid state structures of L-Cys and L-Ser have been determined by neutron diffraction [33,34] and a large number of vibrational spectral studies of Cys and Ser zwitterions are available [35–40], the most recent one being that of Gargaro et al. based on their ROA study [40].

In this chapter, the scale factors of Ala, EtSH and EtOH are generated by fitting their *ab initio* force constants to their respective experimental spectra. The vibrational spectra of Cys and Ser zwitterions are theoretically predicted by transferring the scale factors of Ala for the backbone and EtSH and EtOH for the side chain respectively. A complete set of non-redundant force constants of Cys and Ser are also presented.

## 8.1 Calculations

The *ab initio* force constants and frequencies of Cys, Ser, Ala, EtSH and EtOH were calculated analytically for the optimized geometries at 6-31++G\* level using the Onsager reaction field approach to include the solvent effect. The cartesian force constant matrices were then transformed to the non-redundant local coordinate space. The non-redundant local coordinates of EtSH and EtOH are same as used in chapter 6, that of Ala is given in Table-8.1 and Figure 8.1 and the corresponding Cys and Ser are given in Table-8.2 and Figure 8.2. The optimized geometry of Ala is given in Table-8.3 and those of Cys and Ser are given in Table-8.4. The *ab initio* force fields of Ala, EtSH and EtOH were then fitted to their corresponding experimental spectra to obtain a non-redundant set of force constants and scale factors using the methodology described in chapter 3. We used experimental frequencies from five different isotopomers namely, Ala-d<sub>0</sub>, Ala-Cd<sub>3</sub>, AlaN<sup>+</sup>d<sub>3</sub>, Ala-CdN<sup>+</sup>d<sub>3</sub> and Ala-Cd<sub>3</sub>N<sup>+</sup>d<sub>3</sub> for the present study. Radius of 3.3 Å was used for the solvated model calculation of Ala. The scale factors of EtSH and EtOH along with Ala when used to scale the *ab initio* force fields of Cys and Ser, good agreements were obtained with experimental frequencies. Cavity radii of 3.5 and 3.4 Å were used for the solvated model calculations of Cys and Ser respectively.

## 8.2 Results

### EtSH and EtOH

The most stable gauche form in the isolated EtSH calculation (chapter 6) is retained in the solvated model calculation for the present study at 6-31++G\* level. The ab initio calculated frequencies are fitted to the experimental ones reported in chapter 6. In EtOH again the most staggered conformation is retained as the most stable one in the solvated model calculation, following our earlier EtOH result reported in chapter 6. In condensed phase the presence of intermolecular H-bonding causes a lowering of the  $\nu\text{OH}$  frequency in EtOH. In the present solvated study of EtOH the  $\nu\text{OH}$  frequency is lowered compared to the earlier ab initio calculation on the isolated molecule as expected. We used the same experimental frequencies (as reported in chapter 6) to fit the ab initio calculated frequencies in the present study. The fitted frequencies and their PEDs of both EtSH and EtOH are shown in Table-8.5.

### 8.2.1 Vibrational Frequencies of Ala

The fitted spectra of Ala and its deuterated isotopomers are shown in Tables-8.6 to 8.8. The fitted frequencies are very close to the experimentally observed frequencies for all the five isotopomers considered here with an average deviation of  $7.2\text{ cm}^{-1}$ . The lowest two torsions and the  $\text{NH}_3$  stretching frequencies are omitted from the error calculation. The torsional modes are not well described in the HF calculation [41].

The recent work of Yu et al. based on their Onsager reaction field model ab initio calculation and experimental ROA spectra gives the theoretical assignments of Ala zwitterion in the range  $800$  to  $1600\text{ cm}^{-1}$ . In their study, Yu et al. assigned the  $1613\text{ cm}^{-1}$  band as a mixed mode of  $\nu\text{CO} + \delta_a\text{N}^+\text{H}_3$  followed by  $\delta_s\text{N}^+\text{H}_3$  at  $1503\text{ cm}^{-1}$ . Due to the presence of strong intermolecular H-bonding in the solution phase, the  $\delta_a\text{N}^+\text{H}_3$  mode is expected to appear above  $\nu\text{CO}$ . Earlier Diem et al. [20] assign based on their normal mode analysis both the  $\delta_a\text{N}^+\text{H}_3$  ( $1645, 1625\text{ cm}^{-1}$ ) above  $\nu\text{CO}$  ( $1607\text{ cm}^{-1}$ ). We, in the present study consider  $1645$ ,  $1625$  and  $1613\text{ cm}^{-1}$  bands as the three fundamentals in this region for Ala- $\text{d}_0$ .

In the  $\nu\text{N}^+\text{H}$  and  $\nu\text{CH}$  stretching regions we used experimental frequencies of Diem et al. [20] wherever available. Our assignment matches very well with that of Diem et al. for Ala- $\text{d}_0$ , Ala- $\text{Cd}_3$  and Ala- $\text{N}^+\text{d}_3$ . The agreement between the calculated and experimental bands is excellent in all the modes except that of the highest two  $\nu\text{N}^+\text{H}$ , which were significantly overestimated in the ab initio model calculation. In the solvated model ab initio calculation the intramolecular H-bonding is avoided by putting the molecule in a dielectric continuum and hence the discrepancy in the isolated model (the H-bonded  $\text{N}^+\text{H}$  stretching frequency appearing below  $\nu\text{CH}$ ) is overcome in the present case.

From the VCD spectra it was observed that the difference between the two  $\nu\text{CO}$  stretching bands in Ala- $\text{d}_0$  appear around  $200\text{ cm}^{-1}$  [19]. We assigned the higher  $\nu\text{CO}$  band at  $1613\text{ cm}^{-1}$  and the lower one as a mixed mode at  $1412\text{ cm}^{-1}$ , in agreement with this observation. In the  $1600\text{--}1400\text{ cm}^{-1}$  region we consider the earlier assignment of Diem et al. [20] appears to be the satisfactory ones and our fitted PEDs agree very well with that. In Ala- $\text{d}_0$  we assigned the  $1645$  and  $1625\text{ cm}^{-1}$  bands as  $\delta_\alpha\text{N}^+\text{H}_3$  and  $1503\text{ cm}^{-1}$  band as  $\delta_\beta\text{N}^+\text{H}_3$ . These numbers appear at  $1647$ ,  $1623$  and  $1507\text{ cm}^{-1}$  in Ala- $\text{d}_0$ ,  $1647$ ,  $1622$  and  $1506\text{ cm}^{-1}$  in Ala- $\text{Cd}_3$ ,  $1176$ ,  $1141$  and  $1201\text{ cm}^{-1}$  in Ala- $\text{N}^+\text{d}_3$ ,  $1175$ ,  $1162$  and  $1207\text{ cm}^{-1}$  in Ala- $\text{CdN}^+\text{d}_3$  and  $1178$ ,  $1154$  and  $1200\text{ cm}^{-1}$  in Ala- $\text{N}^+\text{d}_3\text{Cd}_3$  after scaling. Both the  $\delta_\alpha\text{C}_\beta\text{H}_3$  modes are assigned at  $1457\text{ cm}^{-1}$  and are calculated at  $1464$  and  $1458\text{ cm}^{-1}$ . The corresponding  $\delta_\beta\text{C}_\beta\text{H}_3$  appear at  $1359\text{ cm}^{-1}$  and is calculated at  $1375\text{ cm}^{-1}$ . The  $\rho\text{C}_\beta\text{C}_\alpha\text{C}$  mode is assigned at  $1379\text{ cm}^{-1}$  and is calculated at  $1382\text{ cm}^{-1}$ . These two closely spaced bands got exchange during the fitting. Both the  $\delta_\alpha\text{C}_\beta\text{H}_3$  and  $\delta_\beta\text{C}_\beta\text{H}_3$  appeared at  $1044$ ,  $1032$ ,  $1058\text{ cm}^{-1}$  in Ala- $\text{Cd}_3$ ,  $1464$ ,  $1459$ ,  $1377\text{ cm}^{-1}$  in Ala- $\text{N}^+\text{d}_3$  and  $1460$ ,  $1456$ ,  $1372\text{ cm}^{-1}$  in Ala- $\text{CdN}^+\text{d}_3$  and  $1055$ ,  $1043$ ,  $1072\text{ cm}^{-1}$  in Ala- $\text{Cd}_3\text{N}^+\text{d}_3$  in our calculated spectra.

The two  $\rho\text{N}^+\text{H}_3$  modes appear as a mixed modes with  $\rho\text{C}_\beta\text{H}_3$  and  $\delta\text{C}_\beta\text{C}_\alpha\text{C}$  at  $1241$  and  $1147\text{ cm}^{-1}$  for Ala- $\text{d}_0$  after scaling. These two modes are assigned to the experimental bands at  $1238$  and  $1145\text{ cm}^{-1}$  of Susi et al. [5]. These bands get shifted to  $1194$  and  $1155\text{ cm}^{-1}$  in Ala- $\text{Cd}_3$ ,  $887$ ,  $842\text{ cm}^{-1}$  in Ala- $\text{N}^+\text{d}_3$ ,  $846$ ,  $797\text{ cm}^{-1}$  in Ala- $\text{CdN}^+\text{D}_3$  and  $818$ ,  $794\text{ cm}^{-1}$  in Ala- $\text{Cd}_3\text{N}^+\text{d}_3$ . The  $\nu\text{C}_\alpha\text{N}^+$  mode in Ala- $\text{d}_0$  is assigned to the observed band at  $1113$  and  $922\text{ cm}^{-1}$  as a mixed mode with  $\rho\text{C}_\beta\text{H}_3$ ,  $\nu\text{CC}_\alpha$  and  $\nu\text{C}_\alpha\text{C}_\beta$  and are calculated at  $1130$  and  $928\text{ cm}^{-1}$  respectively. The  $\gamma\text{CO}$  and  $\delta\text{COO}$  appear as mixed mode in Ala-

$d_0$  at  $781\text{ cm}^{-1}$  and is calculated at  $796\text{ cm}^{-1}$ . This band is calculated at  $736\text{ cm}^{-1}$  in Ala-Cd<sub>3</sub>,  $782\text{ cm}^{-1}$  in Ala-N<sup>+</sup>d<sub>3</sub>,  $749\text{ cm}^{-1}$  in Ala-CdN<sup>+</sup>d<sub>3</sub> and  $732\text{ cm}^{-1}$  in Ala-Cd<sub>3</sub>N<sup>+</sup>d<sub>3</sub> spectra. The observed band at  $633\text{ cm}^{-1}$  is assigned to a mixed mode of  $\nu C_\alpha C + \delta COO + \nu C_\alpha C_\beta + \gamma CO$  and is calculated at  $640\text{ cm}^{-1}$ . This band is more or less invariant with the isotopic substitution and appear at  $611\text{ cm}^{-1}$  in Ala-Cd<sub>3</sub>,  $612\text{ cm}^{-1}$  in Ala-N<sup>+</sup>d<sub>3</sub>,  $597\text{ cm}^{-1}$  in Ala-CdN<sup>+</sup>d<sub>3</sub> and  $594\text{ cm}^{-1}$  in Ala-Cd<sub>3</sub>N<sup>+</sup>d<sub>3</sub> in our fitted spectra.

### 8.2.2 Vibrational Frequencies of Cys

We transferred all the scale factors from Ala except for the CH<sub>2</sub>SH stretching, bending and torsional modes. The side chain residue is successfully represented by using the scale factors of EtSH. The predicted frequencies of Cys are given in Table-8.9 along with their PEDs. The prediction is in good agreement with the experimental frequencies producing an average error of  $9.0\text{ cm}^{-1}$  for Cys spectra observed bands excluding NH<sub>3</sub> stretchings. Many ambiguities regarding the assignment of vibrational modes, especially in the  $1600\text{--}1400\text{ cm}^{-1}$  region observed in our earlier ab initio calculated results on isolated molecule with simple Durig's scaling [42] are resolved successfully in the present study.

Unlike the isolated model, in the  $\nu N^+H_3$  stretching region, all the N<sup>+</sup>H stretching bands appear above the C <sub>$\beta$</sub> H<sub>2</sub> and C <sub>$\alpha$</sub> H modes as expected. The predicted  $\nu N^+H_3$  frequencies are less than the observed values and the predicted numbers are quite close to that of Ala. The predicted values of both the C <sub>$\beta$</sub> H<sub>2</sub> and the C <sub>$\alpha$</sub> H agree very well with the observed bands of L-Cys and D,L-Cys. The predicted band at  $2947\text{ cm}^{-1}$  ( $\nu C_\beta H_2 + \nu C_\alpha H$ ) agree well with the observed band at  $2935\text{ cm}^{-1}$  in D,L-Cys compared to  $2918\text{ cm}^{-1}$  in L-Cys. The  $\nu SH$  frequency predicted at  $2573\text{ cm}^{-1}$  matches very well with the observed bands of L-Cys and D,L-Cys. The present assignment in this region matches very well with that of Li et al. [39].

In the  $1600\text{ cm}^{-1}$  region the predicted frequencies appear at  $1646$  ( $\delta_\alpha N^+H_3$ ),  $1636\text{ cm}^{-1}$  ( $\nu CO$ ) and  $1599$  ( $\delta_\alpha N^+H_3$ )  $\text{cm}^{-1}$ . This is not in agreement with the gross experimental features of amino acids, namely  $\delta_\alpha N^+H_3$  modes appear above  $\nu CO$ . Changing the basis set and the cavity radii would have resolved this problem. However our aim is to compare the force fields of different amino acids in the same basis set. Surprisingly our predicted

assignment matches exactly with that of Li et al. [39]. The  $\delta_s\text{N}^+\text{H}_3$  band matches well with the experimental frequencies of L-Cys and D, L-Cys and also in agreement with the earlier assignment of Li et al. [39] and Madec et al. [37]. The  $\delta\text{C}_\beta\text{H}_2$  appear as a mixed mode with  $\nu\text{C}_\alpha\text{C}$  at 1431 and 1409  $\text{cm}^{-1}$  in the prediction and agrees quite well with the observed bands of L-Cys and D,L-Cys. The lower  $\nu\text{CO}$  appear as a mixed mode in our predicted spectra at 1431  $\text{cm}^{-1}$  and 1316  $\text{cm}^{-1}$ . This band was earlier assigned at 1400  $\text{cm}^{-1}$  in L-Cys by Li et al. [39] and at 1406  $\text{cm}^{-1}$  by Madec et al. [37] in D, L-Cys spectra. The  $\omega\text{C}_\beta\text{H}_2$  mode is predicted at 1292  $\text{cm}^{-1}$  and are assigned to the observed band at 1296 in L-Cys and at 1308  $\text{cm}^{-1}$  in D,L-Cys. The  $\text{tC}_\beta\text{H}_2$  mode is assigned at 1206  $\text{cm}^{-1}$  in our predicted spectra and agrees well with the earlier assignment at 1203  $\text{cm}^{-1}$  by Madec et al. for L-Cys. Both the  $\rho\text{N}^+\text{H}_3$  modes are predicted at 1144 and 1124  $\text{cm}^{-1}$  and agrees well with the observed bands at 1140  $\text{cm}^{-1}$  in the Raman spectra of L-Cys by Madec et al. [37] and at 1118  $\text{cm}^{-1}$  of L-Cys in the ROA spectra of Gargaro et al. [40]. The  $\nu\text{C}_\alpha\text{N}^+$  mode appear as a mixed mode at 1085 and 934  $\text{cm}^{-1}$  in the predicted spectra and is in agreement with the Ala assignment. These two bands are assigned at 1069 and 936  $\text{cm}^{-1}$  in L-Cys and 1073 and 934  $\text{cm}^{-1}$  in D, L-Cys. The  $\gamma\text{CO}$  mode also appear as a mixed mode in the predicted spectra with  $\delta\text{COO}$  at 881 and 823  $\text{cm}^{-1}$ . This band appear at a higher frequency compared to Ala where it is assigned at 796  $\text{cm}^{-1}$ . The  $\nu\text{C}_\beta\text{S}$  frequency is predicted at 693  $\text{cm}^{-1}$  and agrees very well with the 692  $\text{cm}^{-1}$  band in L-Cys. This band is observed at 657  $\text{cm}^{-1}$  in EtSH spectra. The predicted band at 610  $\text{cm}^{-1}$  is assigned to  $\nu\text{C}_\alpha\text{C}$  and matches very well with the observed band of 615  $\text{cm}^{-1}$  in both L-Cys and D, L-Cys. The lower frequency modes below 400  $\text{cm}^{-1}$  are not available in the experimental spectra and hence our predicted numbers cannot be compared.

### 8.2.3 Vibrational Frequencies of Ser

Same strategy of transferring the scale factors of Ala and EtOH, as in Cys is applied. The predicted frequencies of Ser along with the PED is given in Table-8.10. The agreement is excellent with the zwitterionic frequencies for both L and D,L-Ser with an average error of 10.1  $\text{cm}^{-1}$ . The  $\nu\text{OH}_{(alc)}$  mode appears at 3392  $\text{cm}^{-1}$  in our prediction and the corresponding experimental frequencies are not available. Both the  $\delta_a\text{N}^+\text{H}_3$  bending

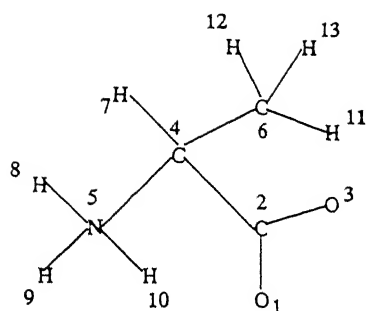
vibrations appear above  $\nu\text{CO}$  followed by  $\delta_s\text{N}^+\text{H}_3$  in our predicted spectra as expected. These modes are predicted at 1645, 1626, 1611 and 1493  $\text{cm}^{-1}$  respectively and agrees very well with our Ala assignment. These bands are not observed in the L-Ser spectra but matches quite well with the D,L-Ser spectra. The  $\delta\text{C}_\beta\text{H}_2$  mode appear at higher frequency compared to that of Cys. This frequency appears at 1460 and 1455  $\text{cm}^{-1}$  in the experimental spectra deviates considerably from the predicted band at 1482  $\text{cm}^{-1}$ . This could be due to the structural variation of  $\text{C}_\beta\text{H}_2$  in Ser and EtOH. The fundamental predicted at 1414  $\text{cm}^{-1}$  is assigned to a mixed mode of  $\omega\text{C}_\beta\text{H}_2$  and  $\delta\text{C}_\beta\text{OH}$  and agrees reasonably well to the observed band at 1430  $\text{cm}^{-1}$  in EtOH spectrum. The  $\text{tC}_\beta\text{H}_2$  mode is predicted at 1275  $\text{cm}^{-1}$  and is in agreement with that of L-Cys predicted value. The predicted band at 1210  $\text{cm}^{-1}$  is also assigned to a mixed mode of  $\omega\text{C}_\beta\text{H}_2$  and  $\delta\text{C}_\beta\text{OH}$  and appear at a lower frequency compared to the experimental ones at 1242 and 1247  $\text{cm}^{-1}$  in L-Ser and D,L-Ser respectively. The corresponding band is observed at 1276  $\text{cm}^{-1}$  in EtOH spectrum. Both the  $\rho\text{N}^+\text{H}_3$  appear at 1187 and 1154  $\text{cm}^{-1}$  as mixed modes in the predicted spectra and matches very well with the observed bands of L-Ser and D,L-Ser. The  $\nu\text{C}_\alpha\text{N}^+$  mode appear at 1093 and 868  $\text{cm}^{-1}$  in the calculated spectra and are observed at 1090 and 851  $\text{cm}^{-1}$  in L-Ser and 1093 and 852  $\text{cm}^{-1}$  in D,L-Ser. The  $\nu\text{C}_\beta\text{O}$  mode is predicted spectra at 1039  $\text{cm}^{-1}$  and agrees well with the observed band at 1040 and 1029  $\text{cm}^{-1}$  in L-Ser and D,L-Ser respectively. This mode was earlier assigned at 978  $\text{cm}^{-1}$  by Machida et al. [36]. The observed band at 978  $\text{cm}^{-1}$  is predicted at 985  $\text{cm}^{-1}$  and is assigned to a mixed mode of  $\rho\text{C}_\beta\text{H}_2 + \rho\text{N}^+\text{H}_3 + \nu\text{C}_\alpha\text{C}_\beta$ . The main discrepancy appear in the observed bands at 773 and 620  $\text{cm}^{-1}$  in the ROA spectra of L-Ser. We do not have any frequency correspond to these in our prediction. The earlier assignment of Ser based on isolated model calculation predicted these two bands at 796 and 615  $\text{cm}^{-1}$  respectively. In the lower frequency range 200-400  $\text{cm}^{-1}$  our predicted frequencies match quite well with the observed D,L-Ser spectra.

The predicted non-redundant force constants of both Cys and Ser and the fitted non-redundant force constants of Ala are given in Tables-8.11 to 8.13.

### 8.3 Conclusions

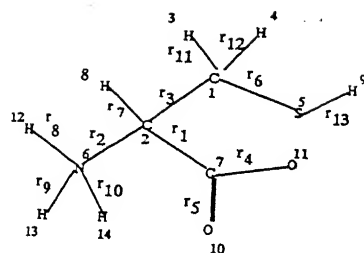
The theoretical prediction of the vibrational spectra of Cys and Ser based on solvated *ab initio* calculation is found to be satisfactory. The scale factors of smallest chiral amino acid, Ala is found to be very useful in predicting the higher chiral amino acids. The present study, led us to infer that the non-redundant set of scale factors of Ala could be used to predict the vibrational spectra of other structurally related amino acids and peptides. However further studies of other amino acids are needed to verify this conclusion. This further implies that the structurally related small organic compounds can be used to mimic the force fields of amino acid side chain residues.



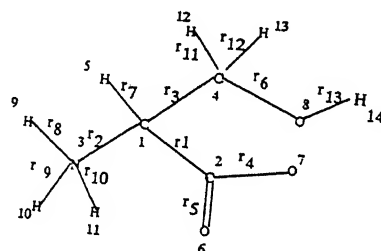


$a=O(1)-C(2)-O(3)$ ,  $a1=C(4)-C(2)-O(1)$ ,  $b1=C(4)-C(2)-O(3)$   
 $a2=C(2)-C(4)-H(7)$ ,  $a3=N(5)-C(4)-H(7)$ ,  $a4=C(6)-C(4)-H(7)$   
 $b2=N(5)-C(4)-C(6)$ ,  $b3=C(2)-C(4)-N(5)$ ,  $b4=C(2)-C(4)-C(6)$   
 $a5=H(8)-N(5)-H(9)$ ,  $a6=H(8)-N(5)-H(10)$ ,  $a7=H(9)-N(5)-H(10)$   
 $b5=C(4)-N(5)-H(8)$ ,  $b6=C(4)-N(5)-H(9)$ ,  $b7=C(4)-N(5)-H(10)$   
 $a8=H(11)-C(6)-H(12)$ ,  $a9=H(11)-C(6)-H(13)$ ,  $a10=H(12)-C(6)-H(13)$   
 $b8=C(4)-C(6)-H(11)$ ,  $b9=C(4)-C(6)-H(12)$ ,  $b10=C(4)-C(6)-H(13)$

Figure 8.1: Internal coordinates of Ala



$a = \text{O}(10)-\text{C}(7)-\text{O}(11)$ ,  $a1 = \text{C}(2)-\text{C}(7)-\text{O}(10)$ ,  $b1 = \text{C}(2)-\text{C}(7)-\text{O}(11)$ ,  $a2 = \text{C}(7)-\text{C}(2)-\text{H}(8)$   
 $a3 = \text{N}(6)-\text{C}(2)-\text{H}(8)$ ,  $a4 = \text{C}(1)-\text{C}(2)-\text{H}(8)$ ,  $b2 = \text{C}(1)-\text{C}(2)-\text{N}(6)$ ,  $b3 = \text{C}(1)-\text{C}(2)-\text{C}(7)$   
 $b4 = \text{N}(6)-\text{C}(2)-\text{C}(7)$ ,  $a5 = \text{H}(12)-\text{N}(6)-\text{H}(13)$ ,  $a6 = \text{H}(12)-\text{N}(6)-\text{H}(14)$ ,  $a7 = \text{H}(13)-\text{N}(6)-\text{H}(14)$   
 $b5 = \text{C}(2)-\text{N}(6)-\text{H}(12)$ ,  $b6 = \text{C}(2)-\text{N}(6)-\text{H}(13)$ ,  $b7 = \text{C}(2)-\text{N}(6)-\text{H}(14)$ ,  $a8 = \text{H}(3)-\text{C}(1)-\text{H}(4)$   
 $a9 = \text{H}(3)-\text{C}(1)-\text{S}(5)$ ,  $a10 = \text{H}(4)-\text{C}(1)-\text{S}(5)$ ,  $b8 = \text{C}(2)-\text{C}(1)-\text{S}(5)$ ,  $b9 = \text{C}(2)-\text{C}(1)-\text{H}(3)$   
 $b10 = \text{C}(2)-\text{C}(1)-\text{H}(4)$ ,  $b = \text{C}(1)-\text{S}(5)-\text{H}(9)$



$a = \text{O}(6)-\text{C}(2)-\text{O}(7)$ ,  $a1 = \text{C}(1)-\text{C}(2)-\text{O}(6)$ ,  $b1 = \text{C}(1)-\text{C}(2)-\text{O}(7)$ ,  $a2 = \text{C}(2)-\text{C}(1)-\text{H}(5)$   
 $a3 = \text{N}(3)-\text{C}(1)-\text{H}(5)$ ,  $a4 = \text{C}(4)-\text{C}(1)-\text{H}(5)$ ,  $b2 = \text{C}(4)-\text{C}(1)-\text{N}(3)$ ,  $b3 = \text{C}(4)-\text{C}(1)-\text{C}(2)$   
 $b4 = \text{N}(3)-\text{C}(1)-\text{C}(2)$ ,  $a5 = \text{H}(9)-\text{N}(3)-\text{H}(10)$ ,  $a6 = \text{H}(9)-\text{N}(3)-\text{H}(11)$ ,  $a7 = \text{H}(10)-\text{N}(3)-\text{H}(11)$   
 $b5 = \text{C}(1)-\text{N}(3)-\text{H}(9)$ ,  $b6 = \text{C}(1)-\text{N}(3)-\text{H}(10)$ ,  $b7 = \text{C}(1)-\text{N}(3)-\text{H}(11)$ ,  $a8 = \text{H}(12)-\text{C}(4)-\text{H}(13)$   
 $a9 = \text{H}(12)-\text{C}(4)-\text{O}(8)$ ,  $a10 = \text{H}(13)-\text{C}(4)-\text{O}(8)$ ,  $b(8) = \text{C}(1)-\text{C}(4)-\text{O}(8)$ ,  $b9 = \text{C}(1)-\text{C}(4)-\text{H}(12)$   
 $b10 = \text{C}(1)-\text{C}(4)-\text{H}(13)$ ,  $b = \text{C}(4)-\text{O}(8)-\text{H}(14)$

Figure 8.2: Internal coordinates of Cys and Ser.

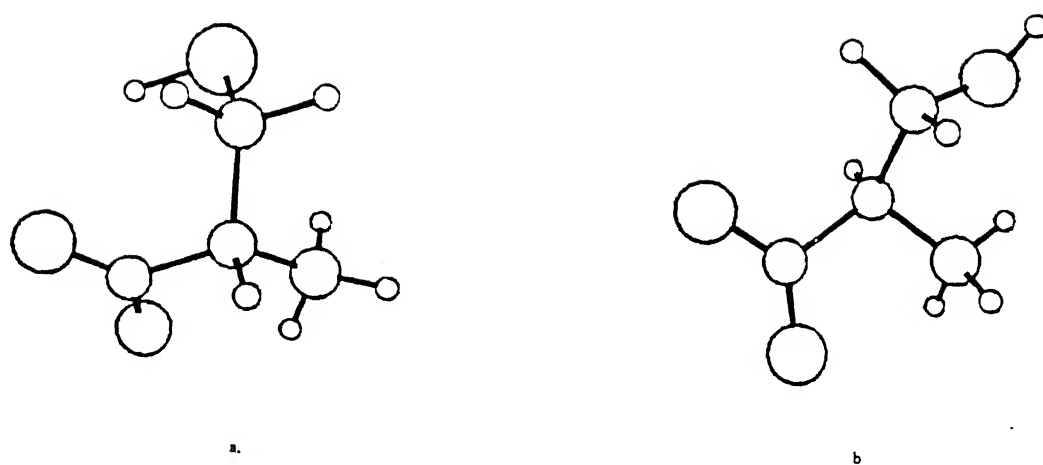


Figure 8.3: Optimized structure of a) Cys and b) Ser at HF/6-31++G\* level.

Table 8.1: Local symmetry coordinates of Ala \*

$S_{1-12}=$	$r_{1-12}(\text{all stretch})$	$S_{23}=$	$2a_7-a_5-a_6(\delta_a N^+H_3)$
$S_{13}=$	$2a-a_1-b_1(\delta COO)$	$S_{24}=$	$a_5-a_6(\delta_a N^+_3)$
$S_{14}=$	$a_1-b_1(\rho COO)$	$S_{25}=$	$a_8+a_9+a_{10}-b_8-b_9-b_{10}(\delta_s C_{\beta}H_3)$
$S_{15}=$	$a_2+a_3+a_4-b_2-b_3-b_4(\delta N^+C_\alpha C)$	$S_{26}=$	$2a_{10}-a_8-a_9(\delta_a C_\beta H_3)$
$S_{16}=$	$2a_2-a_3-a_4(\delta C_\beta C_\alpha C)$	$S_{27}=$	$a_8-a_9(\delta_a C_\beta H_3)$
$S_{17}=$	$a_3-a_4(\rho C_\beta C_\alpha C)$	$S_{28}=$	$2b_8-b_9-b_{10}(\rho C_\beta H_3)$
$S_{18}=$	$2b_2-b_3-b_4(\delta C_\beta C_\alpha H)$	$S_{29}=$	$b_9-b_{10}(\rho C_\beta H_3)$
$S_{19}=$	$b_3-b_4(\rho C_\beta C_\alpha H)$	$S_{30}=$	$\gamma_{4213}(\gamma CO)$
$S_{20}=$	$a_5+a_6+a_7-b_5-b_6-b_7(\delta_s N^+H_3)$	$S_{31}=$	$\tau_{24}(\tau C_\alpha C)$
$S_{21}=$	$2b_5-b_6-b_7(\rho N^+H_3)$	$S_{32}=$	$\tau_{45}(\tau N^+C_\alpha)$
$S_{22}=$	$b_6-b_7(\rho N^+H_3)$	$S_{33}=$	$\tau_{46}(\tau C_\alpha C_\beta)$

\*. Internal coordinate numberings are according to Figure 8.1.

Table 8.2: Local symmetry coordinates of Cys and Ser \*

$S_{1-13}=$	$r_{1-13}(\text{all stretch})$	$S_{25}=$	$a_5-a_6(\delta_a N^+H_3)$
$S_{14}=$	$2a-a_1-b_1(\delta COO)$	$S_{26}=$	$4a_8-a_9-a_{10}-b_9-b_{10}(\delta_s C_\beta H_2)$
$S_{15}=$	$a_1-b_1(\rho COO)$	$S_{27}=$	$a_9+a_{10}-b_9-b_{10}(\omega C_{\beta}H_2)$
$S_{16}=$	$a_2+a_3+a_4-b_2-b_3-b_4(\delta N^+C_\alpha C)$	$S_{28}=$	$a_9-a_{10}+b_9-b_{10}(\rho C_\beta H_2)$
$S_{17}=$	$2a_2-a_3-a_4(\delta C_\beta C_\alpha C)$	$S_{29}=$	$a_9-a_{10}-b_9+b_{10}(tC_\beta H_2)$
$S_{18}=$	$a_3-a_4(\rho C_\beta C_\alpha C)$	$S_{30}=$	$5b_8-a_8-a_9-a_{10}-b_9-b_{10}(\delta C_\alpha C_\beta S/\delta C_\alpha C_\beta O)$
$S_{19}=$	$2b_2-b_3-b_4(\delta C_\beta C_\alpha H)$	$S_{31}=$	$b(\delta CSH/\delta COH)$
$S_{20}=$	$b_3-b_4(\rho C_\beta C_\alpha H)$	$S_{32}=$	$\gamma_{271011}/\gamma_{1267}(\gamma CO)$
$S_{21}=$	$a_5+a_6+a_7-b_5-b_6-b_7(\delta_s N^+H_3)$	$S_{33}=$	$\tau_{12}/\tau_{14}(\tau C_\alpha C_\beta)$
$S_{22}=$	$2b_5-b_6-b_7(\rho N^+H_3)$	$S_{34}=$	$\tau_{15}/\tau_{48}(\tau C_\beta S/\tau C_\beta O)$
$S_{23}=$	$b_6-b_7(\rho N^+H_3)$	$S_{35}=$	$\tau_{27}/\tau_{12}(\tau CC_\alpha)$
$S_{24}=$	$2a_7-a_5-a_6(\delta_a N^+H_3)$	$S_{36}=$	$\tau_{26}/\tau_{13}(\tau C_\alpha N^+)$

\*. Internal coordinate numberings are according to Figure 8.2.

Table 8.3: Optimized geometrical parameters of Ala

param*	Ala	param	Ala	param	Ala
r <sub>1-2</sub>	1.233	a <sub>245</sub>	110.0	a <sub>11612</sub>	108.4
r <sub>3-2</sub>	1.239	a <sub>246</sub>	115.0	a <sub>11613</sub>	108.3
r <sub>4-2</sub>	1.558	a <sub>546</sub>	108.9	a <sub>12613</sub>	108.4
r <sub>5-4</sub>	1.512	a <sub>547</sub>	105.1	$\tau_{3218}$	-168.2
r <sub>6-4</sub>	1.524	a <sub>247</sub>	107.6	$\tau_{1245}$	5.2
r <sub>7-4</sub>	1.082	a <sub>458</sub>	110.4	$\tau_{1246}$	128.5
r <sub>8-5</sub>	1.010	a <sub>459</sub>	112.1	$\tau_{1247}$	-108.8
r <sub>9-5</sub>	1.011	a <sub>4510</sub>	112.6	$\tau_{2458}$	-36.7
r <sub>10-5</sub>	1.015	a <sub>859</sub>	106.1	$\tau_{24611}$	-59.9
r <sub>6-11</sub>	1.086	a <sub>8510</sub>	109.1	$\tau_{2459}$	81.4
r <sub>6-12</sub>	1.081	a <sub>9510</sub>	106.2	$\tau_{24612}$	-158.9
r <sub>6-13</sub>	1.084	a <sub>4611</sub>	111.2	$\tau_{12647}$	-62.0
a <sub>123</sub>	128.4	a <sub>4612</sub>	108.8	$\tau_{11647}$	178.6
a <sub>124</sub>	116.3	a <sub>4613</sub>	111.6	$\tau_{8547}$	78.9
$\tau_{9547}$	-163.0				

\* Internal coordinates are according to Figure 8.1.

Table 8.4: Optimized geometrical parameters of Cys and Ser

param*	Cys	Ser	param	Cys	Ser	param	Cys	Ser
r <sub>1</sub>	1.563	1.552	a <sub>3</sub>	107.7	108.3	b <sub>9</sub>	111.2	110.7
r <sub>2</sub>	1.504	1.504	a <sub>4</sub>	105.9	105.2	b <sub>10</sub>	108.0	108.8
r <sub>3</sub>	1.525	1.526	b <sub>1</sub>	108.7	107.6	$\tau_{6213}/\tau_{31412}$	-55.5	-66.9
r <sub>4</sub>	1.232	1.237	b <sub>2</sub>	110.9	106.4	$\tau_{6215}/\tau_{3148}$	64.1	53.4
r <sub>5</sub>	1.232	1.237	b <sub>3</sub>	114.8	117.5	$\tau_{7213}/\tau_{21412}$	-178.9	58.3
r <sub>6</sub>	1.823	1.392	b <sub>4</sub>	108.5	111.1	$\tau_{7215}/\tau_{2148}$	59.3	178.6
r <sub>7</sub>	1.083	1.082	a <sub>5</sub>	106.7	106.1	$\tau_{8213}/\tau_{51412}$	60.5	-179.2
r <sub>8</sub>	1.014	1.016	a <sub>6</sub>	107.5	107.4	$\tau_{8215}/\tau_{5148}$	-179.9	-58.9
r <sub>9</sub>	1.012	1.007	a <sub>7</sub>	110.0	109.9	$\tau_{12710}/\tau_{4126}$	-42.7	-129.2
r <sub>10</sub>	1.012	1.009	b <sub>5</sub>	107.6	109.8	$\tau_{82710}/\tau_{5126}$	78.4	108.7
r <sub>11</sub>	1.084	1.088	b <sub>6</sub>	111.1	111.6	$\tau_{62710}/\tau_{3126}$	-167.4	-6.3
r <sub>12</sub>	1.078	1.082	b <sub>7</sub>	113.7	111.9	$\tau_{12627}/\tau_{2139}$	-29.7	-62.9
r <sub>13</sub>	1.328	0.952	a <sub>8</sub>	108.0	108.6	$\tau_{12621}/\tau_{4139}$	-156.6	66.1
a	129.9	129.0	a <sub>9</sub>	105.8	104.1	$\tau_{13627}/\tau_{10312}$	86.9	55.8
a <sub>1</sub>	115.0	115.8	a <sub>10</sub>	109.6	112.6	$\tau_{13621}/\tau_{10314}$	-40.0	-175.1
b <sub>1</sub>	115.0	115.2	b <sub>8</sub>	114.0	111.8	$\tau_{2159}/\tau_{14814}$	62.2	-170.3

\* Internal coordinates are according to Figure 8.2

Table 8.5: Fitted frequencies of EtSH and EtOH

no.	EtSH			EtOH			EtOD		
	expt	calc	PED	expt	calc	PED	expt	calc	PED
1	2988	2988	$\nu C(H_2) + \nu C(H_3)$	3336	3437	$\nu OH$	--	2503	$\nu OD$
2	2967	2967	$\nu C(H_3) + \nu C(H_2)$	2975	2975	$\nu C(H_3)$	--	2975	$\nu C(H_3)$
3	2932	2932	$\nu C(H_3)$	2940	2943	$\nu C(H_3)$	--	2940	$\nu C(H_3)$
4	2902	2902	$\nu C(H_2)$	2920	2920	$\nu C(H_2)$	--	2920	$\nu C(H_2)$
5	2875	2875	$\nu C(H_3)$	2890	2890	$\nu C(H_3)$	--	2890	$\nu C(H_3)$
6	2571	2571	$\nu SH$	2877	2877	$\nu C(H_2)$	--	2877	$\nu C(H_2)$
7	1460	1460	$\delta_a CH_3$	1498	1492	$\delta CH_2$	1490	1490	$\delta CH_2 + \delta_a CH_3$
8	1450	1450	$\delta_a CH_3$	1480	1478	$\delta_a CH_3$	1474	1475	$\delta_a CH_3 + \delta CH_2$
9	1434	1434	$\delta CH_2$	1450	1449	$\delta_a CH_3 + \rho CH_3$	1447	1449	$\delta_a CH_3 + \rho CH_3$
10	1376	1376	$\delta_s CH_3$	1430	1446	$\delta COH + \omega CH_2 + \delta CH_2 + \delta_a CH_3$	1401	1401	$\delta_s CH_3 + \omega CH_2 + \nu CC$
11	1273	1273	$\omega CH_2$	1381	1385	$\delta_s CH_3$	1365	1357	$\omega CH_2 + \delta_s CH_3$
12	1251	1251	$t CH_2 + \rho CH_3$	1328	1318	$t CH_2 + \rho CH_3$	1309	1318	$t CH_2 + \rho CH_3$
13	1091	1094	$\rho CH_3 + \delta CSH + t CH_2 + \rho CH_2$	1273	1277	$\omega CH_2 + \delta COH$	1170	1169	$\rho CH_3 + \delta COD + \delta CCO + \nu CC$
14	1052	1052	$\nu CC + \rho CH_3 + t CH_2$	1149	1153	$\rho CH_2 + \rho CH_3 + t CH_2$	1158	1154	$\rho CH_2 + \rho CH_3 + t CH_2$
15	970	970	$\nu CC + \rho CH_3$	1089	1091	$\rho CH_3$	1055	1053	$\nu CO + \nu CC$
16	869	869	$\delta CSH + t CH_2 + \rho CH_3$	1050	1052	$\nu CC + \nu CO$	954	946	$\delta COD + \rho CH_3 + \omega CH_2$
17	737	737	$\rho CH_2 + \rho CH_3 + \delta CSH$	880	887	$\nu CO + \nu CC + \rho CH_3$	877	870	$\nu CO + \nu CC + \rho CH_3$
18	657	657	$\nu CS$	802	800	$\rho CH_3 + \rho CH_2 + t CH_2$	797	799	$\rho CH_2 + \rho CH_3 + t CH_2$
19	319	319	$\delta CCS$	433	439	$\delta CCO + \rho CH_3$	435	429	$\delta CCO + \rho CH_3$
20	247	247	$\tau CC$	260	264	$\tau CO + \tau CC$	--	236	$\tau CC$
21	191	191	$\tau CS$	217	219	$\tau CC + \tau CO$	--	180	$\tau CO + \tau CC$

Table 8.6: Fitted frequencies and PEDs of Ala-d<sub>0</sub>

Ala-d <sub>0</sub>				
no.	unscaled	scaled	expt <sup>a</sup>	PED
1	3734	3124	3080	$\nu\text{N}^+\text{H}_3$
2	3707	3100	3060	$\nu\text{N}^+\text{H}_3$
3	3614	3028	3020	$\nu\text{N}^+\text{H}_3$
4	3324	3015	3003	$\nu\text{C}_\beta\text{H}_3$
5	3288	3005	2993	$\nu\text{C}_\beta\text{H}_3$
6	3271	2961	2962	$\nu\text{C}_\alpha\text{H}$
7	3213	2945	2949	$\nu\text{C}_\beta\text{H}_3$
8	1829	1647	1645	$\delta_\alpha\text{N}^+\text{H}_3$
9	1808	1623	1625	$\delta_\alpha\text{N}^+\text{H}_3$
10	1791	1613	1613	$\nu\text{CO}+\delta_s\text{N}^+\text{H}_3$
11	1672	1507	1503	$\delta_s\text{N}^+\text{H}_3$
12	1636	1464	1457	$\delta_\alpha\text{C}_\beta\text{H}_3$
13	1630	1458	1457	$\delta_\alpha\text{C}_\beta\text{H}_3$
14	1577	1420	1412	$\delta_\alpha\text{C}_\beta\text{H}_3+\nu\text{CO}+\nu\text{CC}_\alpha+\delta_s\text{C}_\beta\text{H}_3$
15	1540	1382	1379 <sup>b</sup>	$\rho\text{C}_\beta\text{C}_\alpha\text{C}$
16	1497	1375	1359 <sup>b</sup>	$\delta_s\text{C}_\beta\text{H}_3$
17	1449	1306	1302	$\delta\text{C}_\beta\text{C}_\alpha\text{C}+\nu\text{CO}$
18	1314	1241	1238 <sup>b</sup>	$\rho\text{N}^+\text{H}_3+\rho\text{C}_\beta\text{H}_3$
19	1221	1147	1145	$\rho\text{N}^+\text{H}_3+\delta\text{C}_\beta\text{C}_\alpha\text{C}$
20	1187	1130	1113	$\nu\text{C}_\alpha\text{N}^++\rho\text{C}_\beta\text{H}_3+\nu\text{C}_\alpha\text{C}_\beta$
21	1050	1023	1003	$\rho\text{C}_\beta\text{H}_3+\rho\text{N}^+\text{H}_3+\rho\text{C}_\beta\text{C}_\alpha\text{C}$
22	1037	1001	995	$\nu\text{C}_\alpha\text{C}_\beta+\rho\text{N}^+\text{H}_3+\rho\text{C}_\beta\text{H}_3$
23	973	928	922	$\nu\text{C}_\alpha\text{N}^++\rho\text{C}_\beta\text{H}_3+\nu\text{CC}_\alpha$
24	891	856	848	$\delta\text{COO}+\nu\text{C}_\alpha\text{N}^++\nu\text{C}_\alpha\text{C}_\beta+\gamma\text{CO}$
25	844	796	781	$\gamma\text{CO}+\delta\text{COO}$
26	642	633	640	$\nu\text{C}_\alpha\text{C}+\delta\text{COO}+\nu\text{C}_\alpha\text{C}_\beta+\gamma\text{CO}$
27	532	525	527	$\rho\text{COO}+\nu\text{C}_\alpha\text{N}^+$
28	422	402	399	$\delta\text{C}_\beta\text{C}_\alpha\text{H}+\delta\text{N}^+\text{C}_\alpha\text{C}$
29	324	318	296	$\delta\text{C}_\beta\text{C}_\alpha\text{H}+\delta\text{N}^+\text{C}_\alpha\text{C}$
30	266	266	283	$\rho\text{C}_\beta\text{C}_\alpha\text{H}+\rho\text{COO}$
31	249	247	219	$\tau\text{C}_\alpha\text{C}_\beta$
32	126	135	184	$\tau\text{N}^+\text{C}_\alpha$
33	58	72	—	$\tau\text{C}_\alpha\text{C}+\tau\text{N}^+\text{C}_\alpha$

a. Ref [19,20] b. Ref. 5.

Table 8.7: Fitted frequencies and PEDs of Ala-Cd<sub>3</sub> and Ala-N<sup>+</sup>d<sub>3</sub>

Ala-Cd <sub>3</sub>			Ala-N <sup>+</sup> d <sub>3</sub>		
scaled	expt <sup>a</sup>	PED	scaled	expt <sup>a</sup>	PED
3124	3080	$\nu\text{N}^+\text{H}$	3015	3003	$\nu\text{C}_\beta\text{H}_3$
3100	3060	$\nu\text{N}^+\text{H}$	3005	2993	$\nu\text{C}_\beta\text{H}_3$
3028	3020	$\nu\text{N}^+\text{H}$	2962	2962	$\nu\text{C}_\alpha\text{H}$
2962	2962	$\nu\text{C}_\alpha\text{H}$	2945	2949	$\nu\text{C}_\beta\text{H}_3$
2239	2251	$\nu\text{C}_\beta\text{D}_3$	2306	2290	$\nu\text{N}^+\text{D}_3$
2229	2236	$\nu\text{C}_\beta\text{D}_3$	2288	—	$\nu\text{N}^+\text{D}_3$
2116	2126	$\nu\text{C}_\beta\text{D}_3$	2176	2160	$\nu\text{N}^+\text{D}_3$
1647	1645	$\delta_\alpha\text{N}^+\text{H}_3$	1605	1608	$\nu\text{CO}$
1622	1625	$\delta_\alpha\text{N}^+\text{H}_3$	1464	1459	$\delta_\alpha\text{C}_\beta\text{H}_3+\rho\text{C}_\beta\text{H}_3$
1612	1615	$\nu\text{CO}+\delta_s\text{N}^+\text{H}_3$	1459	1459	$\delta_\alpha\text{C}_\beta\text{H}_3$
1506	1511	$\delta_s\text{N}^+\text{H}_3$	1416	1409	$\delta_\alpha\text{C}_\beta\text{H}_3+\nu\text{CO}+\nu\text{CC}+\delta_s\text{C}_\beta\text{H}_3$
1421	1414	$\nu\text{CC}+\nu\text{CO}+\delta\text{C}_\beta\text{C}_\alpha\text{O}+\delta\text{COO}$	1377	1376	$\delta_s\text{C}_\beta\text{H}_3$
1378	1360	$\rho\text{C}_\beta\text{C}_\alpha\text{C}$	1365	1355 <sup>b</sup>	$\rho\text{C}_\beta\text{C}_\alpha\text{C}$
1304	1305	$\delta\text{C}_\beta\text{C}_\alpha\text{C}+\nu\text{CO}$	1298	1299 <sup>b</sup>	$\delta\text{C}_\beta\text{C}_\alpha\text{C}+\nu\text{CO}$
1199	1194	$\rho\text{N}^+\text{H}_3+\rho\text{C}_\beta\text{C}_\alpha\text{C}+\nu\text{C}_\alpha\text{C}_\beta$	1201	1193	$\delta_s\text{N}^+\text{D}_3+\nu\text{C}_\alpha\text{N}^+$
1145	1155	$\rho\text{N}^+\text{H}_3+\delta\text{C}_\beta\text{C}_\alpha\text{C}$	1187	—	$\rho\text{C}_\beta\text{H}_3+\nu\text{C}_\alpha\text{C}_\beta+\rho\text{N}^+\text{D}_3$
1120	1128	$\delta_s\text{CD}_3+\nu\text{C}_\alpha\text{C}_\beta+\nu\text{C}_\alpha\text{N}^+$	1176	—	$\delta_\alpha\text{N}^+\text{D}_3$
1058	1066	$\delta_s\text{CD}_3+\delta_\alpha\text{CD}_3+\nu\text{C}_\alpha\text{N}^-$	1149	1161	$\delta_\alpha\text{N}^+\text{D}_3$
1044	1051	$\delta_\alpha\text{CD}_3$	1114	1100	$\rho\text{C}_\beta\text{H}_3+\delta_s\text{N}^+\text{D}_3+\delta\text{C}_\beta\text{C}_\alpha\text{C}$
1032	—	$\delta_\alpha\text{CD}_3\nu\text{C}_\alpha\text{N}^+$	1070	1058	$\nu\text{C}_\alpha\text{C}_\beta+\rho\text{C}_\beta\text{H}_3+\delta_s\text{N}^+\text{D}_3$
950	954	$\nu\text{C}_\alpha\text{C}+\rho\text{N}^+\text{H}_3+\delta_s\text{C}_\beta\text{D}_3+\nu\text{C}_\alpha\text{C}_\beta$	919	922	$\rho\text{C}_\beta\text{H}_3+\nu\text{CC}_\alpha+\nu\text{C}_\alpha\text{N}^+$
930	931	$\rho\text{C}_\beta\text{D}_3+\gamma\text{CO}+\rho\text{N}^-\text{H}_3-\delta\text{N}^+\text{C}_\alpha\text{C}$	887	878	$\rho\text{N}^+\text{D}_3+\rho\text{C}_\beta\text{H}_3+\nu\text{C}_\alpha\text{N}^+$
839	832	$\delta\text{COO}+\rho\text{C}_\beta\text{D}_3$	842	849	$\rho\text{N}^+\text{D}_3+\delta\text{COO}$
777	804	$\rho\text{C}_\beta\text{D}_3+\nu\text{C}_\alpha\text{N}^+$	812	815	$\rho\text{N}^+\text{D}_3+\nu\text{C}_\alpha\text{C}_\beta+\delta\text{COO}+\nu\text{C}_\alpha\text{N}^-$
736	758	$\gamma\text{CO}+\rho\text{C}_\beta\text{D}_3$	782	776	$\gamma\text{CO}+\rho\text{N}^+\text{D}_3$
611	610	$\nu\text{C}_\alpha\text{C}+\delta\text{COO}+\nu\text{C}_\alpha\text{C}_\beta$	612	613	$\nu\text{C}_\alpha\text{C}+\delta\text{COO}$
514	509	$\rho\text{COO}+\nu\text{C}_\alpha\text{C}$	507	513	$\rho\text{COO}+\nu\text{C}_\alpha\text{N}^+$
371	374	$\delta\text{C}_\beta\text{C}_\alpha\text{H}+\delta\text{N}^+\text{C}_\alpha\text{C}$	376	377	$\delta\text{N}^+\text{C}_\alpha\text{C}+\delta\text{C}_\beta\text{C}_\alpha\text{H}$
304	297	$\delta\text{N}^+\text{C}_\alpha\text{C}+\delta\text{C}_\beta\text{C}_\alpha\text{H}+\rho\text{COO}$	304	335	$\delta\text{C}_\beta\text{C}_\alpha\text{H}+\delta\text{N}^+\text{C}_\alpha\text{C}$
246	220	$\rho\text{C}_\beta\text{C}_\alpha\text{H}+\rho\text{COO}$	255	273	$\rho\text{C}_\beta\text{C}_\alpha\text{H}+\rho\text{COO}$
180	191	$\tau\text{C}_\alpha\text{C}_\beta$	247	258	$\tau\text{C}_\alpha\text{C}_\beta+\rho\text{C}_\beta\text{C}_\alpha\text{H}$
134	184	$\tau\text{C}_\alpha\text{N}^+$	105	211	$\tau\text{C}_\alpha\text{N}^++\tau\text{C}_\alpha\text{C}$
70	—	$\tau\text{C}_\alpha\text{C}+\tau\text{C}_\alpha\text{N}^+$	65	184	$\tau\text{C}_\alpha\text{C}+\tau\text{C}_\alpha\text{N}^+$

a. Ref. [19,20] b. Ref. 5.



Table 8.8: Fitted frequencies and PEDs of Ala-CdN<sup>+</sup>d<sub>3</sub> and Ala-Cd<sub>3</sub>N<sup>+</sup>d<sub>3</sub>

Ala-CdN <sup>+</sup> d <sub>3</sub>			Ala-Cd <sub>3</sub> N <sup>+</sup> d <sub>3</sub>		
scaled	expt <sup>a</sup>	PED	scaled	expt <sup>a</sup>	PED
3015	—	$\nu C_\beta H_3$	2962	—	$\nu C_\alpha H$
3004	—	$\nu C_\beta H_3$	2306	—	$\nu N^+ D_3$
2945	—	$\nu C_\beta H_3$	2288	—	$\nu N^+ D_3$
2305	—	$\nu N^+ D_3$	2239	—	$\nu C_\beta D_3$
2288	—	$\nu N^+ D_3$	2229	—	$\nu C_\beta D_3$
2186	—	$\nu C_\alpha D$	2176	—	$\nu N^+ D_3$
2176	—	$\nu N^+ D_3$	2116	—	$\nu C_\beta D_3$
1605	1605	$\nu CO$	1605	1608	$\nu CO$
1460	1460	$\delta_a C_\beta H_3 + \rho C_\beta H_3$	1415	1412	$\nu CC + \nu CO + \delta COO + \delta C_\beta C_\alpha C$
1456	1460	$\delta_a C_\beta H_3 + \rho C_\beta H_3$	1360	1343	$\rho C_\beta C_\alpha C$
1406	1414	$\delta_s C_\beta H_3 + \nu CO + \nu C_\alpha C + \delta COO$	1295	1291	$\delta C_\beta C_\alpha C + \nu CO$
1372	1380	$\delta_s C_\beta H_3 + \nu CO$	1200	1206	$\delta_s N^+ D_3 + \nu C_\alpha N^+$
1235	—	$\nu C_\alpha C_\beta + \rho N^+ D_3$	1178	1175	$\delta_a N^+ D_3$
1207	1212	$\delta_s N^+ D_3 + \nu C_\alpha N^+$	1154	1147	$\delta_a N^+ D_3$
1175	—	$\delta_a N^+ D_3$	1148	—	$\nu C_\alpha C_\beta + \delta_s C_\beta D_3 + \delta_a N^+ D_3$
1162	1159	$\delta_a N^+ D_3 + \rho C_\beta H_3$	1072	1080	$\delta_s C_\beta D_3 + \rho C_\beta D_3 + \nu C_\alpha N^+$
1148	—	$\rho C_\beta H_3 + \delta_a N^+ D_3 + \nu C_\alpha C_\beta$	1055	1057	$\delta_a C_\beta D_3 + \rho C_\beta D_3$
1140	1134	$\delta_s N^+ D_3 + \delta_a N^+ D_3$	1043	—	$\delta_a C_\beta D_3$
1011	1009	$\rho C_\beta C_\alpha C + \rho C_\beta H_3 + \rho N^+ D_3 + \delta C_\beta C_\alpha C$	1027	1026	$\delta_a C_\beta D_3 + \delta N^+ C_\alpha C$
941	944	$\delta C_\beta C_\alpha C + \gamma CO + \nu C_\alpha N^+$	1007	—	$\delta_s C_\beta D_3 + \nu C_\alpha N^+$
901	894	$\nu CC_\alpha + \delta COO + \rho C_\beta H_3 + \nu C_\alpha N^+$	859	857	$\delta COO + \nu C_\alpha C + \rho N^+ D_3$
846	845	$\rho N^+ D_3 + \nu C_\alpha C_\beta + \delta COO$	818	821	$\rho N^+ D_3 + \gamma CO$
826	825	$\rho C_\beta C_\alpha C + \nu C_\alpha C_\beta + \rho C_\beta H_3 + \delta COO$	794	796	$\rho N^+ D_3 + \nu C_\alpha C_\beta + \delta COO$
797	—	$\rho N^+ D_3 + \rho C_\beta C_\alpha C + \nu C_\alpha N^+ + \delta COO$	756	754	$\rho C_\beta D_3 + \nu C_\alpha N^+$
749	—	$\gamma CO + \delta C_\beta C_\alpha C + \rho N^+ D_3$	732	—	$\gamma CO + \rho C_\beta D_3$
597	—	$\nu C_\alpha C + \delta COO + \rho COO$	594	—	$\nu C_\alpha C + \delta COO + \nu C_\alpha C_\beta$
501	—	$\rho COO + \nu C_\alpha N^+$	500	—	$\rho COO + \nu C_\alpha N^+$
374	—	$\delta C_\beta C_\alpha D + \delta N^+ C_\alpha C$	347	—	$\delta N^+ C_\alpha C + \delta C_\beta C_\alpha H$
302	—	$\delta C_\beta C_\alpha D + \delta N^+ C_\alpha C$	284	—	$\delta C_\beta C_\alpha H + \delta N^+ C_\alpha C$
255	—	$\rho C_\beta C_\alpha D + \rho COO$	241	—	$\rho C_\beta C_\alpha H + \rho COO$
247	—	$\tau C_\alpha C_\beta + \rho C_\beta C_\alpha D$	180	—	$\tau C_\alpha C_\beta$
105	—	$\tau C_\alpha N^+ + \tau C_\alpha C$	183	—	$\tau C_\alpha N^+ + \tau C_\alpha C$
65	—	$\tau C_\alpha C + \tau C_\alpha N^+$	64	—	$\tau C_\alpha C + \tau C_\alpha N^+$

a. Ref. [19]

Table 8.9: Predicted frequencies and PEDs of Cys

no.	calc	expt		PED
		L-Cys <sup>a</sup>	D,L-Cys <sup>b</sup>	
1	3108	3167	—	$\nu\text{N}^+\text{H}_3$
2	3099	3167	—	$\nu\text{N}^+\text{H}_3$
3	3034	3055	—	$\nu\text{N}^+\text{H}_3$
4	3003	2998	2989	$\nu\text{C}_\beta\text{H}_2$
5	2960	2960	2976	$\nu\text{C}_\alpha\text{H}+\nu\text{C}_\beta\text{H}_2$
6	2947	2918	2935	$\nu\text{C}_\beta\text{H}_2+\nu\text{C}_\alpha\text{H}$
7	2573	2582	2570	$\nu\text{SH}$
8	1646	—	1663	$\delta_a\text{N}^-\text{H}_3$
9	1636	1616	1628	$\nu\text{CO}$
10	1599	1576	1585	$\delta_a\text{N}^-\text{H}_3$
11	1491	1510	1500	$\delta_s\text{N}^-\text{H}_3$
12	1431	1427	1426	$\delta\text{C}_\beta\text{H}_2+\nu\text{C}_\alpha\text{C}+\nu\text{CO}$
13	1409	1400	1406	$\delta\text{C}_\beta\text{H}_2+\nu\text{C}_\alpha\text{C}$
14	1393	1376	1366	$\rho\text{C}_\beta\text{C}_\alpha\text{C}$
15	1316	1320	1342	$\delta\text{C}_\beta\text{C}_\alpha\text{C}+\nu\text{CO}+\delta\text{COO}$
16	1292	1296	1308	$\omega\text{C}_\beta\text{H}_2+\nu\text{C}_\alpha\text{C}_\beta$
17	1206	1203	1265	$\text{tC}_\beta\text{H}_2+\nu\text{C}_\alpha\text{N}^+$
18	1144	1140	1163	$\rho\text{N}^+\text{H}_3+\delta\text{C}_\beta\text{C}_\alpha\text{C}$
19	1124	1118	1128	$\rho\text{N}^+\text{H}_3+\omega\text{C}_\beta\text{H}_2+\rho\text{C}_\beta\text{C}_\alpha\text{C}$
20	1085	1069	1073	$\nu\text{C}_\alpha\text{N}^++\delta\text{C}_\beta\text{SH}+\rho\text{C}_\beta\text{H}_2+\text{tC}_\beta\text{H}_2$
21	992	990	1000	$\rho\text{N}^+\text{H}_3+\delta\text{C}_\beta\text{SH}+\nu\text{C}_\alpha\text{C}_\beta$
22	934	936	934	$\nu\text{C}_\alpha\text{N}^++\delta\text{C}_\beta\text{SH}+\nu\text{C}_\alpha\text{C}+\nu\text{C}_\alpha\text{C}_\beta$
23	881	875	892	$\gamma\text{CO}+\delta\text{COO}+\delta\text{N}^+\text{C}_\alpha\text{C}$
24	823	823	826	$\delta\text{COO}+\gamma\text{CO}+\delta\text{C}_\beta\text{SH}$
25	792	779	775	$\rho\text{C}_\beta\text{H}_2+\delta\text{C}_\beta\text{SH}+\nu\text{C}_\alpha\text{N}^+$
26	693	692	—	$\nu\text{C}_\beta\text{S}+\gamma\text{CO}$
27	610	615	615	$\nu\text{C}_\alpha\text{C}+\nu\text{C}_\alpha\text{N}^++\delta\text{COO}$
28	543	538	540	$\rho\text{COO}+\rho\text{C}_\beta\text{C}_\alpha\text{H}$
29	495	—	464	$\delta\text{N}^+\text{C}_\alpha\text{C}+\delta\text{C}_\alpha\text{C}_\beta\text{S}+\delta\text{C}_\beta\text{C}_\alpha\text{H}$
30	341	—	—	$\delta\text{C}_\beta\text{C}_\alpha\text{H}+\tau\text{C}_\beta\text{S}+\tau\text{C}_\alpha\text{C}_\beta$
31	327	—	—	$\tau\text{C}_\beta\text{S}+\tau\text{C}_\alpha\text{N}^+$
32	273	—	—	$\tau\text{C}_\alpha\text{N}^++\rho\text{C}_\beta\text{C}_\alpha\text{H}+\tau\text{C}_\beta\text{S}$
33	268	—	—	$\tau\text{C}_\alpha\text{N}^+$
34	187	—	—	$\delta\text{C}_\beta\text{C}_\alpha\text{S}+\tau\text{C}_\alpha\text{C}+\delta\text{N}^+\text{C}_\alpha\text{C}+\tau\text{C}_\alpha\text{C}_\beta$
35	107	—	—	$\tau\text{C}_\alpha\text{C}_\beta+\tau\text{C}_\alpha\text{C}+\nu\text{CO}$
36	91	—	—	$\tau\text{C}_\alpha\text{C}+\tau\text{C}_\alpha\text{C}_\beta$

a. Ref. [39,21] b. Ref [37]

Table 8.10: Predicted frequencies and PEDs of Ser

no.	calc	expt		PED
		L-Ser <sup>a</sup>	D,L-Ser <sup>a</sup>	
1	3392	—	—	$\nu\text{OH}$
2	3160	—	—	$\nu\text{N}^+\text{H}_3$
3	3115	—	—	$\nu\text{N}^+\text{H}_3$
4	3018	—	—	$\nu\text{N}^+\text{H}_3$
5	2971	—	—	$\nu\text{C}_\alpha\text{H}+\nu\text{C}_\beta\text{H}_2$
6	2958	—	—	$\nu\text{C}_\beta\text{H}_2+\nu\text{C}_\alpha\text{H}$
7	2886	—	—	$\nu\text{C}_\beta\text{H}_2$
8	1645	—	1637	$\delta_\alpha\text{N}^+\text{H}_3$
9	1626	—	1626	$\delta_\alpha\text{N}^+\text{H}_3$
10	1611	—	1587	$\nu\text{CO}$
11	1493	—	1523	$\delta_s\text{N}^+\text{H}_3$
12	1482	1460	1455	$\delta\text{C}_\beta\text{H}_2$
13	1438	—	1436	$\nu\text{C}_\alpha\text{C}+\rho\text{C}_\beta\text{C}_\alpha+\nu\text{CO}$
14	1414	1412	—	$\omega\text{C}_\beta\text{H}_2+\delta\text{C}_\beta\text{OH}+\nu\text{C}_\alpha\text{C}_\beta+\nu\text{CC}_\alpha$
15	1381	1390	1377	$\rho\text{C}_\beta\text{C}_\alpha\text{C}+\delta\text{C}_\beta\text{O}$
16	1318	1323	1309	$\delta\text{C}_\beta\text{C}_\alpha\text{C}+\nu\text{CO}$
17	1275	—	—	$\text{tC}_\beta\text{H}_2+\rho\text{N}^+\text{H}_3$
18	1210	1242	1247	$\omega\text{C}_\beta\text{H}_2+\delta\text{C}_\beta\text{OH}$
19	1187	—	1182	$\text{tC}_\beta\text{H}_2+\rho\text{C}_\beta\text{H}_2+\rho\text{N}^-\text{H}_3+\rho\text{C}_\beta\text{C}_\alpha\text{C}$
20	1154	1150	1156	$\rho\text{N}^+\text{H}_3+\delta\text{C}_\beta\text{C}_\alpha\text{C}+\nu\text{C}_\alpha\text{N}^+$
21	1093	1090	1093	$\nu\text{C}_\alpha\text{N}^++\nu\text{C}_\alpha\text{C}_\beta$
22	1039	1040	1029	$\nu\text{C}_\beta\text{O}$
23	985	978	982	$\rho\text{C}_\beta\text{H}_2+\rho\text{N}^+\text{H}_3+\nu\text{C}_\alpha\text{C}_\beta$
24	957	919	—	$\nu\text{C}_\alpha\text{C}+\rho\text{C}_\beta\text{H}_2$
25	868	851	852	$\nu\text{C}_\alpha\text{N}^++\rho\text{C}_\beta\text{H}_2$
26	805	809	815	$\delta\text{COO}+\gamma\text{CO}$
27	687	—	—	$\gamma\text{CO}+\delta\text{C}_\alpha\text{C}_\beta\text{O}+\delta\text{COO}$
28	535	525	528	$\rho\text{COO}+\rho\text{C}_\beta\text{C}_\alpha\text{H}$
29	433	—	—	$\delta\text{C}_\beta\text{C}_\alpha\text{H}+\delta\text{C}_\alpha\text{C}_\beta\text{O}+\nu\text{C}_\alpha\text{C}+\delta_s\text{N}^+\text{H}_3$
30	375	—	383	$\delta\text{C}_\alpha\text{C}_\beta\text{O}+\delta\text{N}^+\text{C}_\alpha\text{C}+\delta\text{N}^+\text{C}_\alpha\text{H}$
31	322	—	324	$\tau\text{C}_\beta\text{O}$
32	291	—	288	$\tau\text{C}_\beta\text{O}+\delta\text{C}_\beta\text{C}_\alpha\text{H}+\delta\text{N}^+\text{C}_\alpha\text{C}+\rho\text{COO}$
33	207	—	222	$\rho\text{C}_\beta\text{C}_\alpha\text{H}+\delta\text{C}_\beta\text{C}_\alpha\text{H}+\rho\text{COO}$
34	170	—	—	$\tau\text{C}_\alpha\text{N}^-$
35	114	—	—	$\tau\text{C}_\alpha\text{C}_\beta+\tau\text{C}_\beta\text{O}$
36	52	—	—	$\tau\text{C}_\alpha\text{C}+\tau\text{C}_\alpha\text{N}^+$

a. Ref. [21]



Table 8.11: (Continued): Ala symbolic F matrix in local coordinates

436 437 438 439 440 441 442 443 444 445 446 447 448 449 450 451  
 452 453 454 455 456 457 458 459 460 461 462 463 464 465  
 466 467 468 469 470 471 472 473 474 475 476 477 478 479 480 481  
 482 483 484 485 486 487 488 489 490 491 492 493 494 495 496  
 497 498 499 500 501 502 503 504 505 506 507 508 509 510 511 512  
 513 514 515 516 517 518 519 520 521 522 523 524 525 526 527 528  
 529 530 531 532 533 534 535 536 537 538 539 540 541 542 543 544  
 545 546 547 548 549 550 551 552 553 554 555 556 557 558 559 560  
 561

## Non-redundant fitted force constants

9.755	1.495	7.882	0.466	0.359	4.139	0.098	-0.003	0.112
4.384	-0.003	-0.004	0.108	0.208	4.358	0.016	0.011	0.053
0.069	0.060	4.818	-0.019	-0.014	-0.033	0.122	-0.002	0.001
5.351	0.009	-0.036	-0.010	0.054	0.009	-0.016	0.022	5.332
-0.011	-0.037	-0.026	0.033	0.003	0.006	0.022	0.027	5.168
0.013	0.016	0.002	0.021	0.066	-0.011	-0.001	-0.001	-0.002
4.913	0.004	0.016	-0.035	-0.007	0.034	0.006	-0.005	-0.007
-0.004	0.049	4.913	0.010	0.001	-0.010	0.015	0.044	0.006
0.003	0.002	0.005	0.048	0.043	4.942	0.226	0.327	-0.450
-0.015	-0.002	-0.009	0.028	0.015	0.032	-0.011	0.013	-0.005
1.497	0.433	-0.351	0.130	-0.242	0.026	0.038	-0.027	-0.012
-0.006	-0.001	0.031	-0.002	-0.078	1.246	-0.001	-0.019	-0.129
-0.148	-0.100	0.095	0.007	0.054	-0.016	0.016	-0.020	-0.012
0.028	0.005	0.968	0.047	0.016	0.143	-0.183	-0.110	0.004
0.013	-0.002	0.014	-0.016	-0.004	0.007	-0.026	0.037	-0.066
0.616	-0.008	-0.007	0.017	0.372	-0.183	0.012	-0.008	0.014
-0.024	-0.027	0.009	0.000	0.006	0.031	0.053	-0.065	0.786
-0.051	-0.017	-0.285	0.277	0.213	0.006	0.052	-0.009	-0.009
-0.001	0.068	-0.014	0.085	0.014	-0.062	-0.046	0.016	1.268
-0.022	0.037	0.149	0.297	-0.181	0.012	-0.052	-0.037	-0.015
-0.008	0.044	-0.021	-0.031	-0.008	-0.206	-0.041	0.046	-0.122
1.277	-0.059	0.040	0.020	-0.245	-0.012	-0.013	0.040	0.077
0.071	-0.009	0.002	-0.004	-0.013	0.058	-0.005	0.026	-0.029
-0.050	0.019	0.565	0.025	-0.052	-0.035	0.000	0.023	0.001
0.082	-0.009	-0.008	-0.004	0.015	-0.007	0.027	-0.006	-0.034
0.007	-0.019	0.089	-0.044	0.015	0.735	0.007	-0.055	-0.012
0.005	-0.003	0.007	0.011	-0.002	0.008	0.016	-0.005	-0.004
0.012	0.017	0.057	-0.029	0.052	0.019	-0.050	0.007	-0.011
0.721	0.004	0.004	-0.004	0.002	0.005	0.000	-0.069	0.051
0.051	0.001	-0.004	0.004	-0.004	-0.001	-0.011	-0.013	-0.002

Table 8.11: (Continued): Ala Symbolic F matrix in local coordinates

0.017	-0.025	0.003	-0.029	0.013	0.605	0.031	-0.028	-0.029
-0.044	0.007	-0.002	0.042	0.066	-0.056	-0.004	0.001	0.000
0.013	-0.029	0.007	0.004	-0.019	0.036	-0.045	0.034	-0.033
-0.001	0.005	0.591	-0.007	-0.023	0.018	-0.034	-0.328	-0.007
-0.002	0.001	0.002	0.073	0.061	0.069	0.005	-0.020	0.017
0.010	0.018	-0.059	0.003	0.010	0.002	-0.001	-0.005	-0.001
0.554	0.020	-0.015	0.009	0.005	-0.010	-0.004	-0.001	-0.003
0.000	-0.111	0.047	0.036	-0.004	-0.005	0.007	0.003	-0.006
-0.019	-0.011	0.000	0.003	0.004	-0.007	-0.001	-0.003	0.534
-0.001	-0.008	0.004	0.005	-0.017	0.000	-0.001	0.002	-0.002
-0.008	0.072	-0.070	0.000	-0.006	0.020	0.004	-0.003	-0.019
-0.017	0.002	0.003	-0.006	-0.003	0.003	0.013	0.010	0.530
-0.011	-0.014	-0.029	-0.055	0.019	0.028	-0.004	0.011	0.001
0.076	-0.054	-0.024	0.006	-0.014	0.084	-0.037	-0.071	-0.061
0.037	0.004	-0.013	0.010	-0.001	-0.001	-0.005	-0.006	-0.014
0.739	-0.034	-0.011	-0.004	0.091	-0.025	0.003	0.000	-0.010
-0.004	0.002	0.101	-0.063	0.014	-0.027	-0.033	0.001	-0.002
0.150	0.061	-0.005	0.030	0.001	-0.002	0.001	0.025	0.020
0.009	0.009	0.673	0.012	0.011	-0.008	0.003	0.033	-0.023
0.009	0.008	-0.003	0.000	0.011	0.001	0.010	0.018	-0.043
-0.060	0.010	-0.023	-0.022	0.004	-0.012	0.003	-0.016	0.002
-0.014	-0.001	0.005	-0.002	-0.012	0.537	-0.012	0.021	-0.029
0.030	0.007	-0.011	-0.044	0.000	0.001	0.004	0.024	-0.003
0.010	0.042	0.061	0.009	0.047	-0.010	0.063	-0.020	0.038
-0.001	0.014	-0.021	0.001	-0.011	0.006	0.003	-0.002	0.043
0.119	-0.026	0.012	-0.016	-0.034	-0.001	0.005	-0.043	-0.018
0.017	-0.001	-0.001	-0.002	0.007	-0.004	0.006	0.010	-0.020
-0.014	0.003	-0.013	0.043	0.002	0.035	0.001	-0.003	-0.001
0.001	0.003	-0.006	0.003	-0.012	0.033	0.004	-0.003	0.022
-0.006	-0.003	0.000	0.001	-0.005	0.002	0.004	0.001	-0.006
-0.005	-0.010	-0.018	0.007	-0.010	-0.015	-0.017	0.000	-0.004
-0.001	-0.002	0.001	0.006	0.017	0.010	0.009	-0.007	-0.009
-0.001	-0.005	0.121						

\* Non-redundant local coordinates are according to Table-8.1.

Table 8.12: Non-redundant scaled force constants of Cys

1	1	4.363																	
2	1	.083	2	4.828															
3	1	.048	2	.031	3	4.837													
4	1	.269	2	.072	3	.041	4	3.086											
5	1	.230	2	-.020	3	-.065	4	-.044	5	4.677									
6	1	.103	2	.011	3	-.007	4	.054	5	.060	6	4.142							
7	1	.060	2	.009	3	.008	4	-.002	5	.065	6	.028	7	4.792					
8	1	-.028	2	-.016	3	.006	4	-.038	5	-.016	6	.035	7	.001					
	8	3.801																	
9	1	-.056	2	-.023	3	.000	4	.125	5	-.132	6	.450	7	.011					
	8	.001	9	9.710															
10	1	-.072	2	.036	3	.031	4	.206	5	-.061	6	.466	7	.008					
	8	.014	9	1.424	10	8.331													
11	1	-.046	2	.007	3	-.016	4	-.082	5	.229	6	.068	7	-.001					
	8	-.005	9	.081	10	-.135	11	4.921											
12	1	.010	2	.000	3	-.005	4	-.049	5	.102	6	.014	7	-.011					
	8	-.001	9	-.041	10	.009	11	.031	12	5.229									
13	1	.000	2	.012	3	-.001	4	-.098	5	.093	6	.022	7	.008					
	8	-.006	9	.007	10	-.009	11	.018	12	.031	13	5.147							
14	1	-.008	2	-.012	3	.003	4	-.016	5	-.013	6	-.579	7	.000					
	8	-.007	9	.240	10	-.051	11	.001	12	.007	13	.006	14	1.488					
15	1	-.002	2	.094	3	.068	4	-.010	5	.160	6	-.241	7	-.041					
	8	-.004	9	.261	10	-1.052	11	-.264	12	.016	13	-.104	14	.175					
	15	1.458																	
16	1	-.255	2	.006	3	.011	4	.025	5	-.342	6	-.144	7	.079					
	8	.084	9	-.040	10	.362	11	-.137	12	-.059	13	-.302	14	.064					
	15	-.053	16	1.161															
17	1	-.089	2	.102	3	.106	4	.009	5	-.233	6	.147	7	-.108					
	8	.037	9	-.038	10	.056	11	.146	12	.084	13	.199	14	-.038					
	15	-.030	16	-.085	17	.667													
18	1	-.153	2	-.048	3	-.047	4	-.059	5	.389	6	-.005	7	.055					
	8	-.020	9	-.160	10	-.307	11	.088	12	.020	13	.064	14	-.026					
	15	-.020	16	.012	17	-.081	18	.767											
19	1	.171	2	-.126	3	-.056	4	.022	5	.172	6	-.350	7	.030					
	8	.064	9	-.188	10	-.091	11	-.687	12	.152	13	-.299	14	.102					
	15	.027	16	-.008	17	-.041	18	.000	19	1.461									
20	1	.316	2	.205	3	.128	4	.008	5	-.488	6	-.328	7	-.044					
	8	-.044	9	-.090	10	-.580	11	-.545	12	.115	13	-.186	14	.085					
	15	.126	16	.212	17	.005	18	-.057	19	.214	20	1.673							

Table 8.12: (Continued): Non-redundant scaled force constants of Cys

21	1	-.007	2	-.003	3	.005	4	-.002	5	-.312	6	.039	7	-.011																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																											</
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Table 8.12: (Continued): Non-redundant scaled force constants of Cys

31	1	.004	2	.017	3	-.002	4	.198	5	-.010	6	.008	7	-.005
	8	-.205	9	.039	10	-.003	11	-.006	12	-.004	13	-.002	14	-.008
	15	-.002	16	-.033	17	.008	18	.008	19	-.019	20	.030	21	.001
	22	.004	23	.000	24	-.001	25	.001	26	-.020	27	.054	28	.071
	29	.105	30	-.014	31	.871								
32	1	-.004	2	-.030	3	-.036	4	-.018	5	.006	6	.015	7	.034
	8	-.034	9	.202	10	-.269	11	-.020	12	-.024	13	-.016	14	.001
	15	.051	16	.040	17	.048	18	.008	19	.020	20	-.015	21	-.007
	22	.006	23	-.003	24	.006	25	-.023	26	.003	27	.000	28	.001
	29	.010	30	.017	31	-.003	32	.460						
33	1	.037	2	.383	3	.452	4	.170	5	.033	6	.058	7	.052
	8	.171	9	-.418	10	-.035	11	-.185	12	.022	13	-.095	14	-.061
	15	.003	16	.027	17	.038	18	-.025	19	.072	20	-.030	21	.001
	22	-.019	23	-.001	24	.010	25	-.038	26	.015	27	.041	28	.054
	29	.036	30	-.037	31	.031	32	-.004	33	.379				
34	1	.007	2	-.003	3	-.002	4	.033	5	.015	6	.007	7	-.002
	8	-.086	9	-.024	10	-.028	11	.007	12	.009	13	.009	14	-.002
	15	.007	16	-.022	17	.001	18	-.001	19	-.024	20	.009	21	-.002
	22	.011	23	.001	24	-.010	25	.007	26	.006	27	.005	28	-.039
	29	.012	30	.020	31	.039	32	-.008	33	.020	34	.099		
35	1	.010	2	.034	3	.061	4	.036	5	-.002	6	-.066	7	-.029
	8	.036	9	-.753	10	-.787	11	-.104	12	-.044	13	-.094	14	-.082
	15	-.002	16	.030	17	.007	18	.095	19	.029	20	-.045	21	-.016
	22	-.004	23	-.014	24	-.002	25	-.040	26	-.003	27	.019	28	.029
	29	.017	30	.049	31	.014	32	.003	33	.057	34	-.008	35	.363
36	1	-.009	2	-.002	3	.002	4	.027	5	-.059	6	-.036	7	.007
	8	.006	9	.010	10	-.014	11	-.731	12	-.227	13	-.570	14	.008
	15	.057	16	.045	17	-.038	18	-.048	19	.080	20	.061	21	-.039
	22	-.110	23	-.068	24	.007	25	-.137	26	.000	27	-.004	28	.044
	29	.009	30	-.032	31	-.001	32	.013	33	.056	34	.009	35	.054
	36	.357												

\* Non-redundant local coordinates are according to Table-8.2.





Table 8.13: (Continued): Non-redundant scaled force constants of Ser

31	1	.026	2	.001	3	.008	4	.354	5	.018	6	-.012	7	.003
	8	.021	9	.000	10	-.019	11	.002	12	.001	13	-.004	14	.014
	15	.002	16	-.004	17	-.003	18	.006	19	-.006	20	.026	21	-.007
	22	-.008	23	-.017	24	.001	25	-.002	26	.007	27	-.005	28	-.003
	29	-.001	30	.067	31	.805								
32	1	-.020	2	-.002	3	-.009	4	-.005	5	-.009	6	-.004	7	.022
	8	-.010	9	-.016	10	-.016	11	-.005	12	.000	13	-.001	14	-.010
	15	-.001	16	.044	17	.059	18	-.006	19	.031	20	-.029	21	.000
	22	-.009	23	.006	24	-.009	25	-.009	26	.000	27	.004	28	-.003
	29	.000	30	-.015	31	-.001	32	.514						
33	1	-.111	2	.007	3	.004	4	-.011	5	.024	6	.024	7	-.011
	8	-.005	9	.000	10	-.002	11	.003	12	.007	13	.019	14	-.003
	15	-.016	16	-.045	17	.045	18	.005	19	-.118	20	.023	21	-.011
	22	.004	23	.002	24	-.032	25	-.016	26	.002	27	.011	28	-.097
	29	-.021	30	-.082	31	-.016	32	.013	33	.230				
34	1	-.037	2	.006	3	.002	4	-.024	5	.005	6	.000	7	-.003
	8	-.007	9	.027	10	-.029	11	-.004	12	-.001	13	.008	14	.001
	15	-.006	16	.021	17	.012	18	-.008	19	-.027	20	.010	21	.001
	22	-.003	23	-.003	24	.000	25	.005	26	.002	27	.006	28	-.071
	29	-.022	30	-.046	31	.007	32	-.003	33	.051	34	.044		
35	1	-.009	2	-.002	3	-.017	4	.020	5	-.006	6	.002	7	.012
	8	-.005	9	.020	10	-.027	11	-.007	12	.018	13	.002	14	-.003
	15	-.034	16	-.058	17	-.010	18	-.042	19	.008	20	.030	21	.006
	22	.022	23	-.015	24	.008	25	.020	26	-.008	27	.001	28	-.003
	29	.000	30	-.004	31	.000	32	.032	33	.003	34	-.002	35	.090
36	1	-.035	2	.003	3	.004	4	-.014	5	.002	6	.004	7	.003
	8	-.005	9	.010	10	-.004	11	.007	12	.016	13	-.040	14	-.003
	15	.002	16	-.006	17	-.001	18	.007	19	-.019	20	.011	21	-.006
	22	.001	23	-.050	24	.056	25	.065	26	-.002	27	.004	28	-.004
	29	.004	30	-.022	31	.000	32	.006	33	-.001	34	.001	35	-.028
	36	.058												

\* Non-redundant local coordinates are according to Table-8.2.

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## Chapter 9

# Conclusions and Future Scope

The availability of a number of empirical force fields and their popularity in getting useful chemical and biochemical insights clearly demonstrate the necessity of having a dependable force field for the molecules of interest. It has been shown that adjusting the empirical parameters to reproduce the experimental vibrational frequencies have significant improvement on the inferences made from the simulations. Ab initio force fields having a firm theoretical basis is expected to provide more reliable parameters than the empirical ones. To this end, in this thesis we proposed an alternative methodology for scaling the ab initio force constants. The resulting scaled quantum mechanical force field in terms of a complete set of non-redundant force constants is utilized for interpretation and prediction of the vibrational spectra of few organic molecules and amino acids. The results show that the methodology works as good as other known scaling procedures and better in few favourable cases.

In the case of organic molecules many well studied systems are available in the literature. We used some of them like acrolein, benzene, naphthalene etc. to interpret their vibrational spectra. By transferring the scale factors from structurally related molecular systems the predictive ability of the present methodology has been tested for few molecules like pyridine, benzaldehyde and anthracene. The final results suggest the general applicability of the scaling methodology. A set of reliable non-redundant scaled force constants have been obtained for all the organic molecules studied. However incorporating these parameters, into simulation of molecular mechanics and dynamics is deferred for future work.



The use of ab initio methods to describe the vibrational characteristics of amino acids is still in its infancy. The nature of intermolecular H-bonding present in the condensed phase poses serious problems in mimicking the experimental features of vibrational spectra using ab initio calculations on isolated molecules. Different ways of incorporating this environmental effect into calculations involving single molecule are explored. Single molecular calculation on hydrochlorides of amino acids and Onsager reaction field approach of immersing the molecule in a dielectric continuum on amino acid zwitterions are found to give reasonably good results. A complete set of non-redundant force constants were obtained for the amino acids and their hydrochlorides investigated in this thesis. To incorporate these results into molecular mechanics simulations require the data for other amino acids, work in this direction is in progress in our laboratory.

## List of Publications :

1.Theoretical study of the ground state vibrations of methoxydifluorophosphine-d<sub>0</sub> and d<sub>3</sub>

D.Chakraborty and S.Manogaran, *J.Mol.Struct.(THEOCHEM)*, 1993, 284, 163.

2.Ground state vibrations of N-glycylglycine hydrochloride - An ab initio study

D.Chakraborty, A.Yash and S.Manogaran, *J.Mol.Struct.(THEOCHEM)*, 1994, 303, 265.

3.Ground state vibrations of guanidinium and methylguanidinium ions - An ab initio study

D.Chakraborty, and S.Manogaran, *Indian J. Chem.*, 1994, 33A, 969.

4.Force field and assignment of vibrational spectrum of anthracene - Theoretical prediction.

D.Chakraborty, R.Ambashta and S.Manogaran, *J.Phys.Chem.*, 1996 100, 13693

5.Accurate prediction and interpretation of vibrational spectra - a modified ab initio scaled quantum mechanical approach

S.Manogaran and D.Chakraborty, *J.Phys.Chem.*, manuscript under revision.

6. Theoretical prediction of vibrational spectra of N-glycylglycine hydrochloride - An ab initio study

D.Chakraborty and S.Manogaran *J.Phys.Chem.*, manuscript under revision.

7. Vibrational analysis of glycine zwitterion - An ab initio study

D.Chakraborty and S.Manogaran, *J.Phys.Chem.*, manuscript under revision.

8.Groud state vibrational spectra of cystien and serine hydrochloride - A Theoretical

prediction

D.Chakraborty and S.Manogaran, *J. Mol. Struct.(THEOCHEM)* submitted.

9.An accurate prediction and interpretation of vibrational spectrum of L-cystiene and L-serine - An ab initio study

D.Chakraborty and S.Manogaran, Manuscript under preparation.

CMM-1996- D-CHA-GRO